CATALYSIS

OF

AMMONOLYTIC REACTIONS

by

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Approved by:

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For several years a striking analogy has been known to exist between the properties of hydrogen ion in water solution, and those of ammonium ion in ammonia solution. For instance, both affect indicators in the same way, and both dissolve some metals with the evolution of hydrogen. Such analogies led Dr.H.P.Cady to believe that ammonium ion might be a catalyst for reactions in liquid ammonia in which ammonia is taken up or lost, as hydrogen ion is a catalyst for reactions in water solution, in which water is taken up or lost. This investigation was undertaken with the purpose of finding out whether or not this is the case.

Reactions in water solution in which water is taken up or lost are called hydrolytic reactions; and Dr.E.C.Franklin of Leland Stanford University has suggested that the analogous name "ammonolytic" be applied to reactions taking place in liquid ammonia solution in which ammonia is taken up or lost.

Hydrolysis of esters by acids in water solution furnished the subject of some of the classic work in chemical statics and dynamics; ammonolysis of esters seemed to be a promising field for investigation.

Since the choice of particular reactions for study depended largely on the ease with which the necessary quantitative measurments could be made, considerable preliminary work was done along this line, with the result that the only reaction studied in a really quantitative way was that

between ammonia and ethyl iodide. Qualitative experiments have been made on the reactions of ammonia with each of the following: amyl oxalate, ethyl acetate, and ethyl formate. These will be discussed first, under the head of "Reactions of the esters of carboxylic acids".

REACTIONS OF THE ESTERS OF CARBOXYLIC ACIDS

AMYL OXALATE

Although the following experiments are only qualitative in nature, being originally intended as preliminary to a quantitative study of the reaction, it is believed that the results are consistent enough to warrant inclusion in this paper.

Two small test tubes, with equal amounts of amyl oxalate in the bottom and corked to prevent the entrance of ammonia gas, were cooled in a Dewar tube of liquid ammonia. The oxalate froze. An ammonia solution on ammonium nitrate was made in a small Dewar tube; a pipette-full of ammonia was added to one of the oxalate tubes and a pipette-full of ammonia solution of ammonium nitrate to the other. Both were vigorously stirred to dissolve the crystalline amyl oxalate. Oxamid formed at once in the body of the solution containing ammonium nitrate, and along the sides of the other test tube, which were wet with amyl oxalate above the level of the bath, and exposed to the gaseous ammonia. Stirring thus assured that in both

tubes there was no chance for supersaturation with respect to oxamid; but while cloudiness appeared at once in the tube containing ammonium nitrate, it was several minutes later in the other one. Since the two were side by side in the same bath, the temperature must have been very nearly the same in the two tubes, but temperature was not determined.

Experiment 2.

Qualitative determination of the effect of water and of ammonium nitrate on the rate of formation of oxamid.

A wire rack was made to suspend four test tubes in the Dewar tube bath. Six drops of amyl oxalate was frozen in each and at the time noted in each case, a pipette-full of ammonia or ammonia solution of ammonium nitrate was added.

Tube 1 Ammonia and amyl oxalate.

Time mixed: 4:33:34. Seeded with oxamid at 4:43, but did not cloud the solution. Cloudiness appeared at 4:50. The precipitate seemed to settle out in fairly large particles as fast as formed, so the solution did not appear very cloudy.

Tube 2 Ammonia, amyl oxalate, and 10 drops of water.

Time mixed: 4:35. Cloudy from the start, as the mass of amyl oxalate apparently left oxamid on disintegration. At about 4:49 the cloud began to agglomerate in larger particles, Well developed strings of oxamid were present at 4:53. By 4:58 the solution was nearly clear of the fine cloud.

Tube 3 A weak solution of ammonium nitrate in ammonia and amyl oxalate.

Time mixed:4:38:39. Suspected the formation of a precipitate at 4:45. Seeded with oxamid at 4:47, which left the solution quite cloudy. Large particles were plain at 4:51, but not so numerous as in tube 2. At 4:53, the solution was largely clear showing only rapidly settling large particles.

Tube 4 Strong solution of ammonium nitrate in ammonia, and amyl oxalate.

Time mixed:4:41:42, precipitating oxamid immediately. At 4:51, strings had formed in the scratches on the tube, but the solution was still cloudy at 4:53.

Final results at 5:05 Tube 2 was probably nearly complete.No. 1 had about 1/10 as much precipitate as No.2, No 3 about 2/3 as much, No.4 at least 9/10 as much.Negative results were obtained in tests for oxalate as ion in the residues of all the tubes.

The preceeding experiments were then repeated with some variations as indicated. One drop of water was weighed out into a test tube and equivalent quantities of ammonium chloride, ammonium nitrate,and sodium nitrate weighed out into others, and each dissolved in fifteen c.c. of ammonia. This was done in tubes cooled in an ammonia bath in a Dewar tube. Six drops of amyl oxalate was then cooled in each of four test tubes,and then five c.c. of one of the ammonia solutions added.

DATA

1. .0416 grams H_2O. 2. .1234 grams NH_4Cl.

3. .1848 grams NH_4NO_3. 3. .1964 grams $NaNO_3$.

Tube 1. Water solution added at 5:35. Precipitate plainly visible at 5:42. It was still slight at 5:45, being less than in 2 and still less thaniin 3. At 5:50, there were trees of oxamid and the solution was largely clear except for the larger particles. At 5:55, 1 was the clearest of the solutions, 2 and 3 were about equal.

Tube 2 Ammonium chloride solution added at 5:37. At 5:42 there was more precipitate than in one. Trees were forming at 5:43 and were prominent at 5:50, when the cloud was giving place to larger particles. At 5:55 2 and 3 were about equal in depth of precipitate, which was much greater in these than in either 1 or 4. At 6:05 there did not seem to be any more precipitate in either 2 or 3 than there was at 5:55.

Tube 3. Ammonium nitrate solution added at 5:39:1/2. Strongly clouded at 5:44.Trees had begun to show at 5:45 and were well developed at 5:50 but the solution was not as well cleared as 2. For later readings, see other tube records, especially 2.

Tube 4. Sodium nitrate solution added at 5:43. The first precipitate appeared at 5:47 but it was on the bottom of the test tube instead of the usual cloudiness. At 5:52 there was

the usual cloudy appearance, with the beginnings of trees. Using the depth of precipitate in #4 as a standard at 6:04, "1 was 1½ or 2 and #2 and #3 each 3 in depth. At 6:10 they were keeping the same order, but there was no more precipitate in #2 and #3 than at 6:04. #1 had nearly as much as these and #4 more than half as much. At 6:15 all four of the solutions were about equally clear and of the same general appearance except that there did not seem to be more than three fourths as much precipitate in #4 as in the others. The results might be summarized to show how long it took to show a precipitate, how long before the trees began to form, and how long before the reaction was apparently over.

SUMMARY OF DATA

Time required for--

Salt used.	First ppt.	Formation of trees	Complete Reaction.
H_2O	7 min.	15 min.	35-40 min
NH_4Cl	5 "	8 "	18 "
NH_4NO_3	4½ "	5½ "	15 "
$NaNO_3$	4 " (?)	9 "	32 plus.

The results of this experiment combined with those preceeding, seem to indicate that in a qualitative way that ammonia reacts with amyl oxalate considerably more rapidly in the presence of an electrolyte, and that in equivalent concentrations, ammonium chloride and ammonium nitrate are more active catalyzers than water or sodium nitrate.

The experiments were never carried out in a quantitative stage because no analytical plan suggested itself which could compare in ease and accuracy with the conductivity method used in the experiments on ethyl iodide.

ETHYL ACETATE

Several attempts were made to study the reaction of ethyl acetate and ammonia by the conductivity method used with ethyl iodide but they failed, because the acetamide formed in this reaction is a weak acid and so poor an electrolyte in ammonia solution that it was impossible to follow the rate of the reaction in this way. Even if it had been found possible to measure the rate of the reaction without the presence of an ammonium salt, the addition of an ammonium salt to determine the effect of the ammonium ion on the rate of reaction would have caused trouble in two ways. In the first place, a very small concentration of an ammonium salt would have a conductivity greater than a large concentration of acetamide, and so would drown out the effect of a small change in concentration of acetamide on the conductivity. Secondly, the degree of ionization of the weak acid acetamide would be very greatly decreased by the presence of the strong acid, the ammonium salt.

The conductivity method was abandoned for these reasons, and the attempt was made to measure directly the quantity of acetamide formed in parallel experiments, under as near the same conditions as possible, with an ammonium salt dissolved in one solution but not in the other.

Preliminary experiments which it is unnecessary to describe indicated that the reaction between anhydrous ammonia and ethyl acetate is very slow, even at ordinary temperatures. Therefore a constant temperature bath was constructed, which operated at 42.8 degrees C., and the samples allowed to react at this temperature for a week.

April 25, 1921

Data

Dry ammonia was distilled into the bombs, which rested in a bath of liquid ammonia cooled below its boiling point by continyous removal of ammonia vapor with a suction pump. The samples were then weighed in from a light dropping funnel in the case of liquids, or from a weighing bottle in the case of solids. It was the intention to get equal concentrations of ethyl iodide in the two samples. That this was very nearly accomplished, is shown by the weights and volumes. Bomb #1 contained 4.57 grams of ethyl acetate; the liquid depth was six inches. Bomb #2 contained 4.19 grams of ethyl acetate and one gram of NH_4Br; the liquid depth was 5.6 inches.

After sealing off the tubes, each was put in a piece of gas pipe, and the gas pipe was set in the 42.8 degree thermostat, where they were allowed to remain for a week. Except for the first night, when the regulating devise stuck and allowed the temperature to rise to nearly 70 degrees, con-

stant temperature was maintained.

Treatment of sample #1, which did not contain NH_4Br.

The gas-pipe bomb containers were removed from the thermostat to a pail of ice-water. After cooling, the bombs were removed from the safety containers, and put into Dewar tubes of liquid ammonia, just as had been done to fill them. After the application of suction had lowered the temperature of the ammonia in the bomb sufficiently, the tip was broken off of the bomb, which was then clamped out in open air to evaporate. The evaporation of the ammonia causes the formation of a heavy sheath of ice on the bomb, whose insulating effect prevents heat from reaching the ammonia fast enough to cause dangerous bumping. When most of the ammonia had evaporated, the residue was washed into a small distilling flask with pure dry benzene, and distilled up to 100 degrees over a gauze. The residue was not quite free from benzene, as was shown by its odor, but the odor of mice had appeared in the distillate. The residue was not homogeneous, but had a drop of a heavier brown liquid below the main portion, which was clear. On cooling, however, all solidified, giving white crystals, slightly brown in the lower part. The weight of the residue, which seemed to be acetamide in its general properties, such as odor and solubility, was .2797 grams. The nitrogen content was not determined because of the diffi-

culties encountered in the treatment of sample #2, which seemed to make comparisons and conclusions difficult.

Treatment of sample #2, which contained NH_4Br. After the ammonia was evaporated off from sample #2, the residue was shaken with benzene. Two liquid layers were formed and NH_4Br was precipitated. The upper layer was mainly benzene and free from bromides; the lower layer contained NH_4Br. The upper layer was pipetted out, and the residue again shaken with benzene. This was repeated several times, then the benzene extractions were distilled up to 140 degrees, about 40 degrees higher than in the case of #1. This was done because of the persistence of the odor of benzene in the distillate. There was unquestionably some acetamide lost, as some condensed in the side-tube of the distilling flask; but, worse, the heat caused the formation of a large quantity of a dark brown substance. The residue weighed .5117, or nearly twice the weight of the residue from #1. The residue crystallized, but was much darker than that from #1, and odor of mice that is associated with impure acetamide more pronounced.

In view of the fact that the residues of both #1 and #2 had been distilled to a sufficiently high temperature to insure freedom from ammonia, ethyl acetate and alcohol, and that the odor of benzene was nearly gone, the conclusion

that these residues consisted mostly of acetamide, seems fairly well warranted, with out the conclusive evidence that an analysis would have given.

At the time this experiment was done, a great deal of time was spent in the examination of the lower layer formed when the residue from the evaporation of the ammonia was shaken with benzene, which would have been more profitably spent on the upper layer.

Afew drops of the liquid of the lower layer was used for each of the following tests: positive test for bromides with silver nitrate and nitric acid; positive test for alcohol by the iodoform reaction; a brown instead of a blue coloration with copper sulfate when the test for water was applied.

The remainder of the liquid was pipetted into a small weighed distilling flask; its weight was .8255 grams. It was distilled up to 194 degrees, when the residue fumed strongly. It was extracted six times with warm benzene, until cooling no longer precipitated acetamide. The remaining liquid still gave the brown coloration with anhydrous copper sulfate. If a drop of water was added to this brown copper sulfate, there was a slight indication of the separation of yellow crystals. Water was added to the whole of the residue; the water solution merely turned copper sulfate blue. The water solution wasdistilled up to 180 degrees, when it seemed to undergo considerable decomposition, with the formation of a brown substance. On

cooling, a very few fine white crystals separated out, which were supposed to be NH_4Br, but were not tested because of the exceedingly small quantity. The whole residue weighed .4325 grams, had a pronounced odor of mice, and turned anhydrous copper sulfate brown.

Acetone was added to this residue. It precipitated a white solid, which was filtered off and dried. Water solution of this solid did not give a test for bromine with silver; nor more than a slight coloration in the Nessler test for ammonia. The solid while wet with the acetone mother-liquor turned copper sulfate brown. An attempt to determine the melting-point of the solid showed that it was unaffected by a temperature of 280 degrees, which leads to a suspicion that the solid may have been a small quantity of some inorganic substance other than a salt of ammonium or bromine.

Further investigation was impossible, because the last of the solid was used in the attempted melting-point determination.

The acetone solution from which the solid was separated left on evaporation two or three tenths of ac.c. of a liquid with a strong odor of mice, which refused to crystallize at zero degrees.

The experiment was unsatisfactory in many ways. The determination of the quantity of acetamide produced should

have been the main object of the experiment; but it was lost sight of in the examination of the lower layer formed with benzene.

The conclusions from this experiment are: that more acetamide is probably formed when the ammonia contains NH_4Br, and that quite certainly, more impurities are formed; that another experiment should be conducted under such circumstances that the acetamide formed could be quantitatively determined; that distillations should be carried out under conditions which would prevent the excessive local heating which takes place when a small quantity of a liquid is heated in a distilling flask over a gauze.

Because of lack of time, no more experiments were conducted on ethyl acetate. Ethyl formate was substituted, because preliminary experiments had shown that the reaction between ammonia and ethyl formate takes place very much more rapidly than the reaction with the acetate.

ETHYL FORMATE

The following experiment with ethyl formate will be described, although it is not in any way conclusive.

Sample #1 contained 2.9782 grams of ethyl formate; sample #2 contained 3.4065 grams of ethyl formate, and 1.0 grams of ammonium bromide. The volumes were in this case not the same, there was a liquid depth of 4½ inches in #1 and 3¾ in #2. The bombs were filled in the same way described

under ethyl acetate, sealed off and put in the gas-pipe containersin the 42.8 degree thermostat over night, then cooled in ice, removed from the gas-pipe, cooled in ammonia, and the tips broken off. The ammonia was allowed to evaporate off of #1, which was then poured out into a weighed beaker, and the bomb washed out with dry acetone. #2 was treated similarly, except that a large excess of acetone was added, in order to completely precipitate the ammonium bromide, and then allowed to settle. The acetone was then evaporated on the water bath, and the attempt was made to heat to constant weight, but both samples fumed readily, and this proved impossible. The weights given are those at the appearance of the first fume. The residue from #1 weighed 1.8331, and from #2, 3.6424.

The residues would not freeze in an ice-salt mixture, either alone, or after shaking with ether, i nwhich they are not soluble. The residue from #1 was oily, not very viscous, slightly red in color, much heavier than ether, insoluble in ether, soluble in water; water solution gave a negative test for ammonia with Nessler's solution, but gave a heavy white precipitate. Concentrated KOH converts the amide into ammonia. The residue from #2 was exceedingly viscous, of about the color of bromine; water solution gave a negative test for ammonia with Nessler's solution, but gave a heavy white precipitate. Concentrated KOH converted the amide to ammonia, leaving the substance causing the red coloration as a gummy

mass, soluble in ether and in HCl, giving red solutions in each case. No further attempt was made to identify the red gum, but from the analyses given below, it seems probable that it contained no nitrogen.

ANALYSES OF THE PRODUCTS

The regular Kjeldahl determination was made on a sample of each of the residues from the evaporation of acetone. #1 gave 28.76 % N, and #2, 15.32 % N. The percentage of N calculated for formamid is 31.11. Since this determination was made before the fact was noted that hydrolysis of #2 with concentrated KOH left a residue, it was thought possible that the sample might have partially volatilized without b being attacked by the sulfuric acid, so direct distillation wi with alkali was resorted tosince amide nitrogen can be freed as ammonia in this way. The results, however, were lower than by the Jjeldahl method: 25.30 % N in #1, and 12.44 % N in #2. Perhaps distillation was not carried on long enough to drive over all of the amide nitrogen as ammonia, but it is clear that sample #2 was not over half formamide.

Figuring the percentage yields on the basis of the weights of the residues, and the Kjeldahl determinations of nitrogen calculated as formamide, #1 gave 94.5 %, and #2, 86.5 % of theoretical yield. The analyses are not good enough to say that the above yields are right; the attempted evaporation to constant weight showed that the loss

by evaporation was in the neighborhood of 1 % per minute, and it is entirely possible that the true yield was in each case 100 %, and that the rest was lost on heating.

Therefore, no conclusion can be drawn as to the effect of the ammonium salt on this reaction, beyond saying that the yield of impurities seemed to be increased. If a little more time had been available, another experiment would have been conducted, in which the ammonia and ethyl formate were allowed to react for a shorter time at a lower temperature, thus stopping the reaction when not more than half of the ethyl formate had reacted.

As was stated in the beginning, the results of the reactions of the esters of the carboxylic acids and ammonia are to be considered as qualitative only, and as indicating to some extent, the nature of the quantitative experiments which should follow.

REACTION OF ETHYL IODIDE AND AMMONIA

By far the greatest part of the time has been spent in the study of this reaction. It was chosen for the reason that a highly ionized salt, ammonium iodide, is formed in the reaction, which makes it possible to follow the course of the reaction continuously by mesuring the conductance of the solution. The main disadvantage found in the use of this reaction, is that it is undoubtedly complicated by side and

successive reactions. This much has been proved concerning the nature of the products: that there is practically no primary amine formed, nor any secondary; and that distillation with solid KOH gave some tertiary amine, which may have come from the decomposition of tetra ethyl ammonium iodide. Whatever the mechanism of the reaction, on mole of an ammonium salt appears for each mole of ethyl iodide used up. The ammonium salt may be substituted; it may be either the hydoiodide of triethyl amine, or tetra ethyl ammonium iodide. But any hydroiodide of triethyl amine must be accompanied by at least two moles of ammonium iodide formed along with it; and probably by much more as in an ammonia solution, the law of mass action would indicate that most of the HI formed should combine with ammonia rather than with the amine which is present in very small concentration. No mesurements of triethyl amine salts' conductivities seem to have been made, but Franklin and Kraus [a] measured the conductivities of ammonium chloride, diethyl ammonium chloride, and ethyl ammonium chloride, and found them very nearly the same.

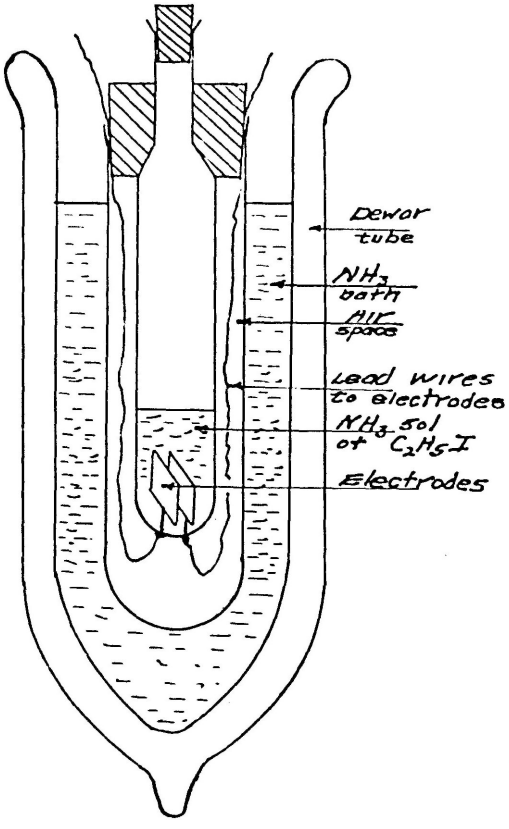
[a] Franklin and Kraus, Am. Chem. Jr. 23, 290, Table VII and Jr. Am. Chem. Soc., 27, 199, Tables LXVI and LXVII.

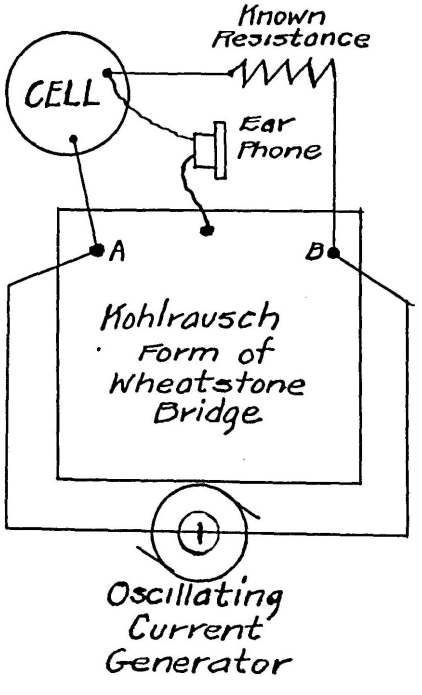
If any of the quaternary salt were formed in the reaction, it of course could not dissociate into the corresponding amine and let ammonium ion crry the charge; but it would be accompanied by three times as many equivalents as was remarked before, of ammonium iodide.

PRELIMINARY EXPERIMENTS ON ETHYL IODIDE

Two typical experiments will be described here, out of a dozen or so that were run, since these show sufficiently the conclusions which were drawn from the series.

Adiagram of the apparatus is shown below.





The electrodes were of platinum, about two centimeters in area, and about three millimeters apart. The platinum leads were sealed through the cell, and soldered to copper wires which made the exterior connections. The cell did not rest directly in the ammonia of the bath, but in a test tube. This was necessary to protect the leads. The electrical resistance was measured with the Kohlraush form of the Wheatstone bridge, in which the slide wire is wound around a cylinder. The measuring current was from an oscillating generator, and the balance was determined with a telephone.

The proceedure was as follows: ammonia was drawn into the Dewar tube, and the cell, inside its protecting test tube, was set into the ammonia. Ordinary ammonia with no purification was then drawn into the cell until the electrodes were covered about a quarter of an inch . The sample of ammonia was then weighed in from a dropping pipette, the cell corked up and thoroughly agitated to insure thorough mixing of the ethyl iodide. Resistance measurements were then made at intervals of half-minutes or minutes for twelve hours. Whenever the ammonia in the bath ran low, more was drawn into it. Special attention should be given to the results of this change of conditions.

Resistances as determined from the Wheatstone bridge data was corrected for the resistance of the line with the electrodes short-circuited, and the corresponding conductances calculated.

The following readings were chosen from several hundred taken, taking those which an inspection of the curve of all the data showed would give substantially the same curve.

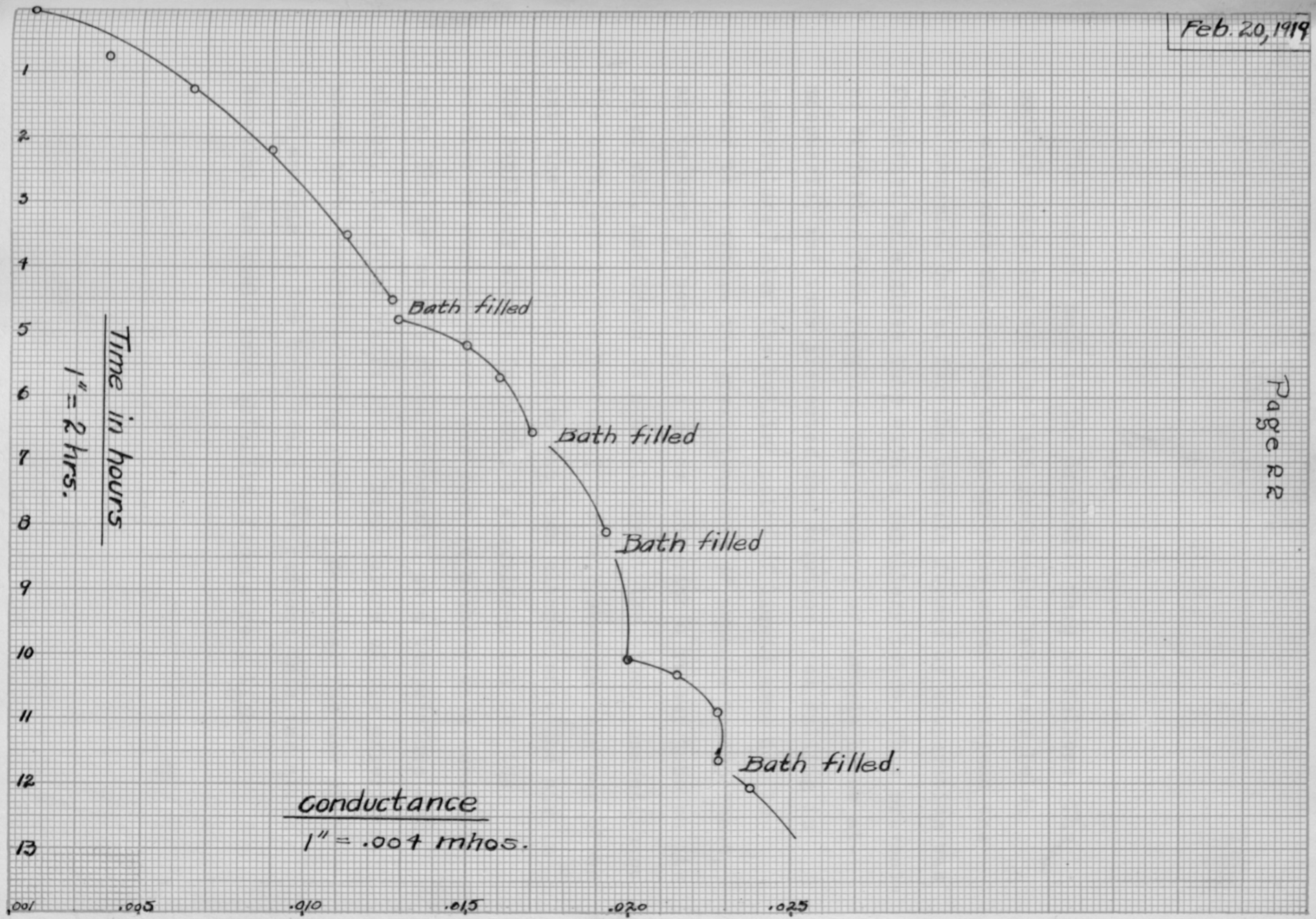
TABLE OF SELECTED DATA FROM THE EXPERIMENT OF FEB.20, 1919

BOX RES.	BRIDGE	TOTAL RES	CELL RES.	COND'ANCE	TIME
610	503	617.4	614.8	.001627	0
200	500	200	1974	.005066	:45
170	1748	153.7	151.1	.006618	1:15
110	5058	112.58	109.98	.009093	2:11
90	5037	9134	88.74	.01307	3:24
83	4942	81.10	78.50	.01274	4:29
Filled up cooling bath with ammonia					
83	4905	79.91	77.31	.01294	4:37
69	5000	69.00	66.40	.01506	5:14
66	4959	64.92	62.32	.01605	5:43
62	4970	61.26	58.66	.01705	6:33
Filled cooling bath with ammonia					6:35
55	4972	54.39	51.79	.01931	8:07
Filled cooling bath with ammonia					10:00

BOX RES.	BRIDGE	TOTAL RES.	CELL RES.	COND'ANCE	TIME
52	4966	51.30	48.70	.02053	10:03
52	4851	4899	46.39	.02156	10:19
46	5022	46.42	43.82	.02282	10:54
46	5022	46.42	43.82	.02282	11:40
Filled cooling bath with ammonia					
46	4923	44.63	42.03	.02379	12:01

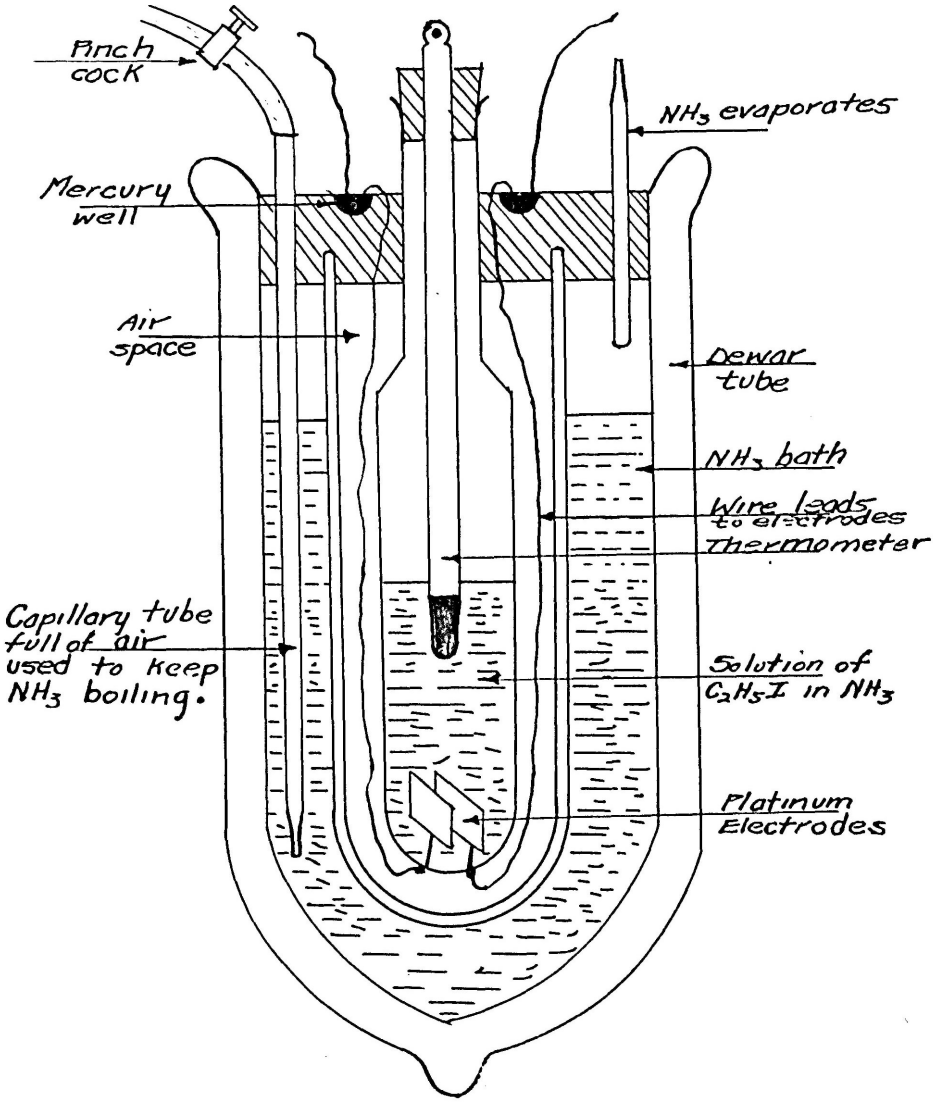
The curve on the following page shows conductance plotted against time for this experiment. The great increase in conductance which took place every time ammonia was drawn i into the bath, evidently makes this experi ment useless as far as getting any notion of the order of the reaction is concerned. It simply showed that the temperature of the bath was not a constant, and that changes of bath temperature had as much to do with the changes of conductance observed as did the formation of electrolyte, and that temperature must be kept constant in later experiments.

Feb. 20, 1919


Time in hours
1" = 2 hrs.
1
2
3
4
5
6
7
8
9
10
11
12
13
Bath filled
Bath filled
Bath filled
Bath filled.
Conductance
1" = .004 mhos.
.001
.005
.010
.015
.020
.025

The changes made in the apparatus were as follows. The cork in which the cell and its protecting tube were held, was also made to cork up the Dewar tube which contained the bath ammonia. Outlet for the ammonia formed by evaporation was furnished by a glass tube with a capillary point. This prevented diffusion from reducing the pressure of ammonia below atmospheric, and thus prevented the solution from falling in temperature below the boiling point of liquid ammonia. In order to overcome the great tendency of ammonia to superheat, and to keep it boiling, a glass tube with a rubber tube on its outer end, and drawn to a capillary at the other, passed throu the cork, and to the bottom of the bath ammonia. Air was blown into the rubber tube, which was then clamped off. The air in the capillary always furnished a starting-point for the bubbles of ammonia vapor, and kept it boiling at a constant rate. The devise was quite successful as a temperature regulator, the total variation in temperature of the experiment about to be described being about .3 degrees. The use of pure ammonia in the bath could have reduced this variation somewhat, as could have shielding from strong light.

Following is a diagram of the improved cell.

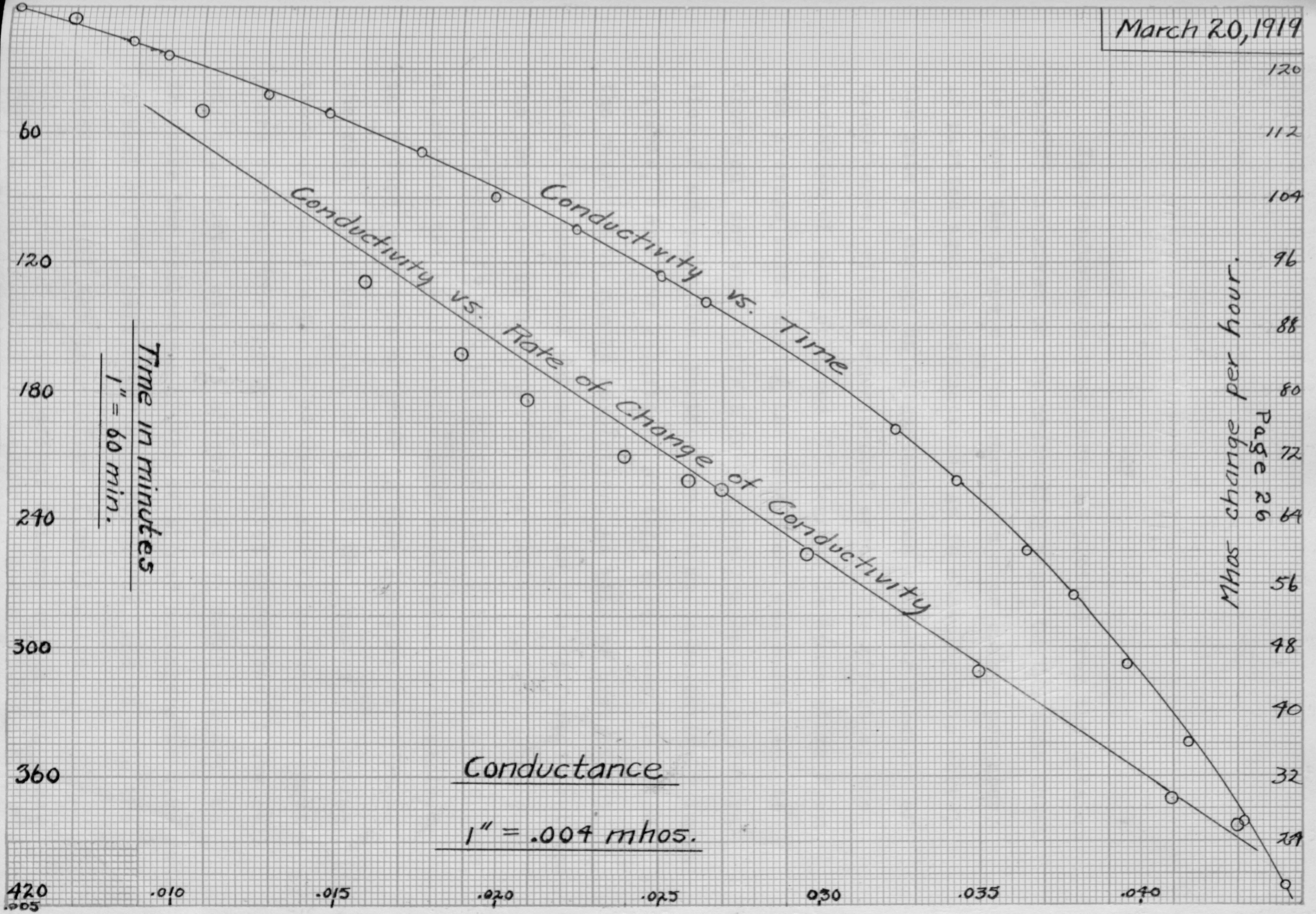


As in the former experiment, readings were taken every minute or half minute, when possible. The temperature was read at frequent intervals during the seven and one half hours the experiment ran. As before, the data here given is selected from over four hundred readings, as giving substantially the same curve of conductance vs. time as all the data.

SELECTED DATA FROM THE EXPERIMENT OF MARCH 20, 1919

TEMP.	RES. BOX	BRIDGE	RES.TOTAL	CELL RES.	COND'ANCE	TIME
-35	200	4897	192.2	191.7	.00522	0
33.3	120	4870	114.1	113.6	.00882	19
33.1	110	4798	101.3	100.8	.00993	25
33.02	80	4906	77.00	76.54	.01305	42
33.09	70	4904	67.40	66.94	..01494	52
33.08	60	4856	56.70	56.24	.01778	70
33.05	50	4982	49.65	49.19	.02033	89
33.25	50	4927	44.80	44.34	.02252	106
33.08	41	4953	40.25	39.79	.02512	127
3302	39	4941	38.15	37.69	.02653	139
33.14	32	4951	31.35	30.89	.03238	200
33.13	32	4810	29.64	29.18	.03428	224
33.27	29	4902	27.90	27.44	.03645	256
33.30	27	4990	26.85	26.39	.03790	278
33.30	27	4876	25.72	25.26	.03960	308
33.20	25	4954	24.55	24.09	.04150	345
33.18	24	4957	23.60	23.14	.04325	382
33.18	24	4892	22.95	22.50	.04450	412
33.18	22	5012	22.10	21.65	.04625	461

March 20, 1919



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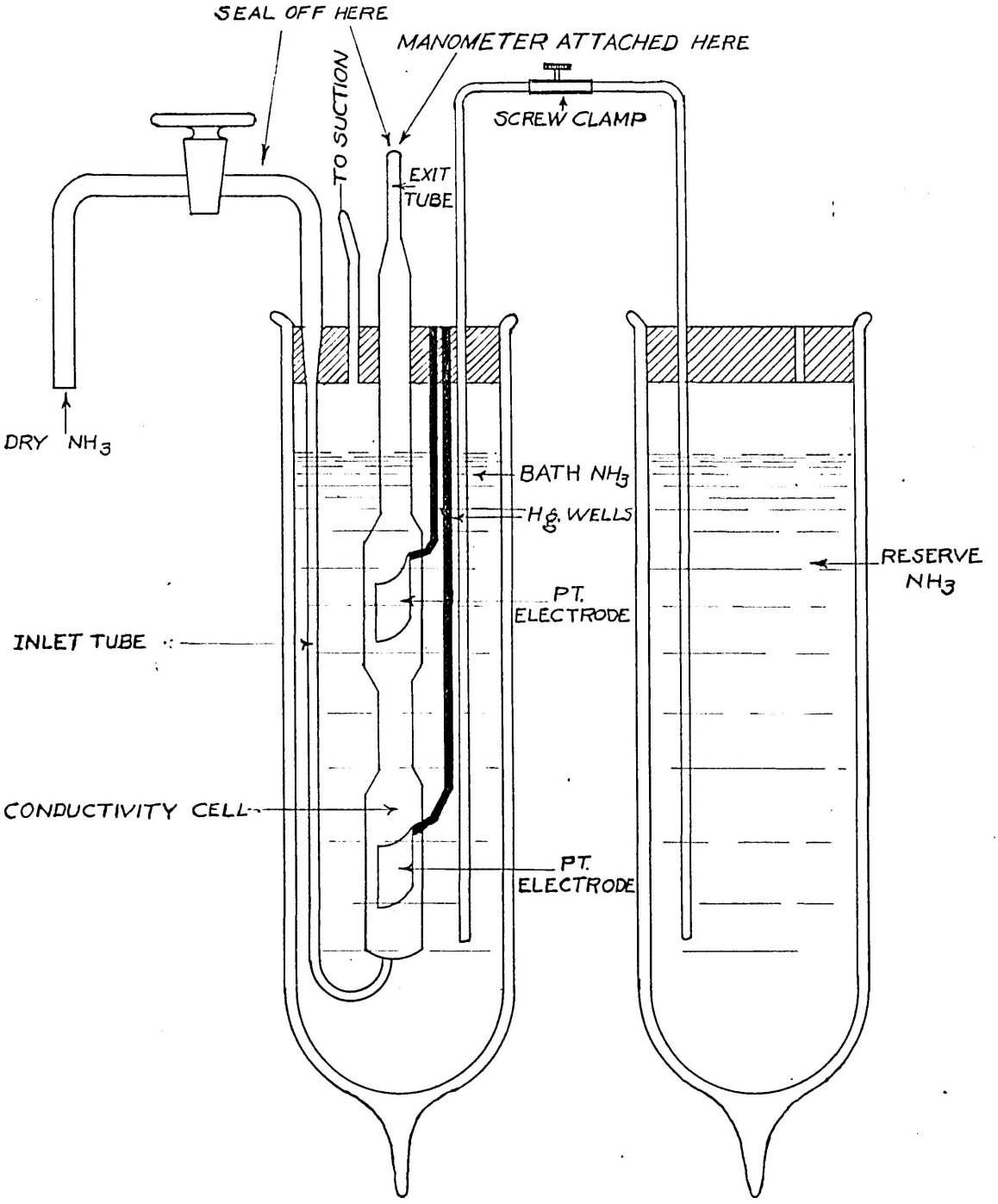
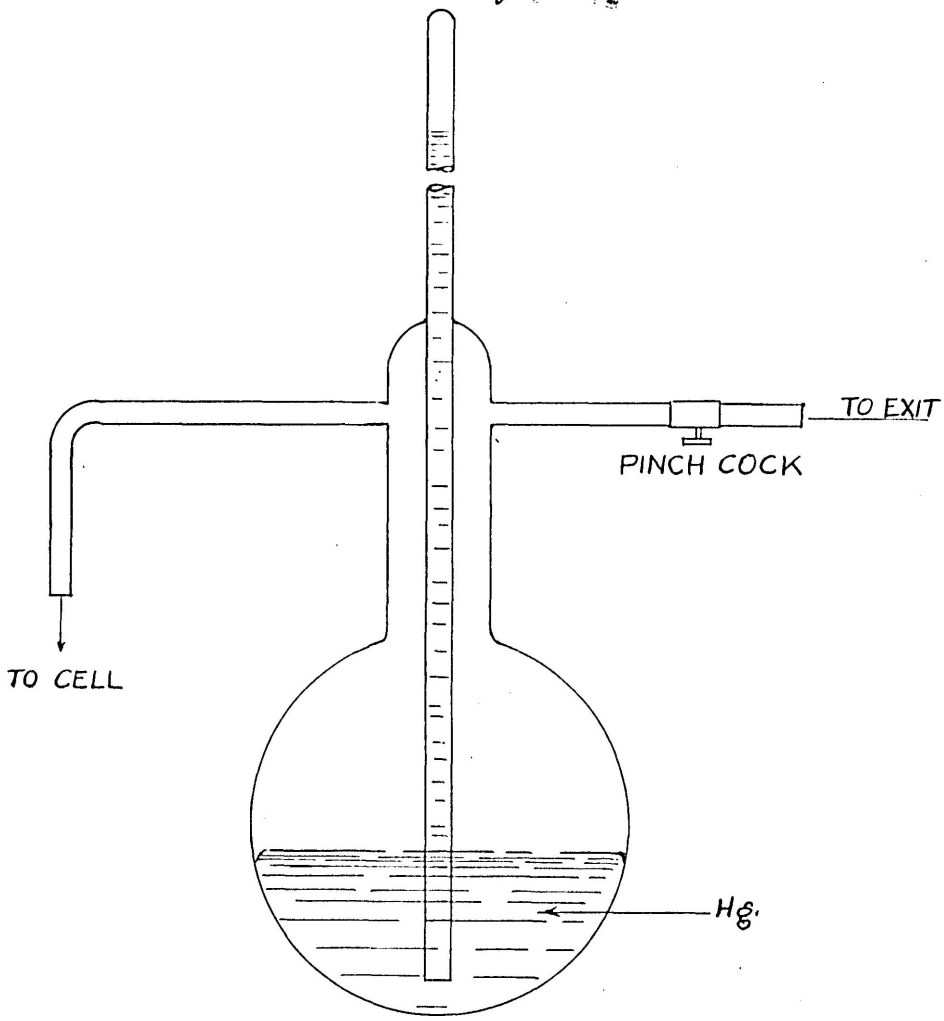
The conductance-time curve as plotted from the data on page 25, is given on the preceeding page. On the same sheet is shown the slope of this curve, in mhos change per hour, is plotted against conductance. As is shown by this curve, the rate of change of conductance was a linear function of conductance, within experimental error. The effect of the variation of plus or minus .15 degrees in temperature from the average value during the experiment was sufficient to drown out any small effect due to the increasing concentration of ammonium ion. Furthermore, it would be entirely impracticable, under the conditions of this experiment, to allow the reaction to run to completion. As will be brought out later, the graphical method depends on the difference between the instantaneous and the final values of the conductances.

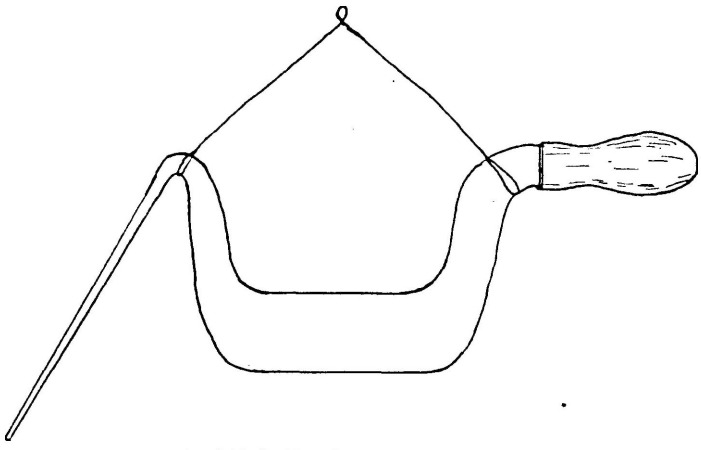
In order to meet the difficulties pointed out above, and to magnify the possible effect of catalysis, the experimental method had to be modified in such a way as to increase the rate of the reaction, to permit the greater concentrations of ammonium ion to be used, and to get better temperature control. The problem was solved as follows. A new cell was constructed with the electrodes much farther apart, to increase the resistance of the cell; and arrangements were made to seal off the cell when ready for a run, and to make the measurements at the temperature of melting ice.

A diagram of this apparatus follows on the next page.


SEAL OFF HERE
MANOMETER ATTACHED HERE
TO SUCTION
SCREW CLAMP
EXIT TUBE
DRY NH3
BATH NH3
Hg. WELLS
RESERVE NH3
PT. ELECTRODE
INLET TUBE
CONDUCTIVITY CELL
PT. ELECTRODE



MANOMETER



WEIGHING PIPETTE

PREPARATION OF MATERIALS

Pure anhydrous ammonia was obtained as follows: ordinary ammonia was distilled out of the stock cylinder into a smaller one which contained over a pound of sodium, cut into small pieces. Connection between the cylinders was made by means of a lead pipe. When a little ammonia had distilled over the small cylinder was disconnected and blown off, to get rid of the air which originally filled it. It was then replaced and filled. Later developments showed that it was filled too full, as the valve stuck due to the precipitation of insoluble sodamide while leaning against a wall. This could not have happened if the ammonia level had not been up in the valve. On removal of the valve to clean it, a stream of liquid ammonia shot out with greatviolence. Disturbing as this was at the time, it turned out to be of advantage later, as the hydrogen which was formed from the reaction of the sodium with the water was all removed.

Pure ethyl iodide was prepared by fractional distillation, the fraction used boiling at a practically constant temperature of 72.3 degrees. It was perfectly clear when prepared, but darkened slightly from liberated iodine later, although kept in the dark. It was not considered necessary to repurify it.

EXPERIMENTAL PROCEEDURE

Ordinary ammonia was drawn into the Dewar tube to act as the cooling bath, and a reserve supply was drawn into another, so arranged that ammonia from it could be drawn over into the bath to replace the loss by evaporation. The rubber stopper carrying the cell fitted the Dewar tube well. The inlet tube from the reserve ammonia supply ran from the bottom of the one Dewar tube to that of the other, with a rubber tube connection between the two, so that a screw clamp could be used to control the admission of ammonia to the bath. Exit for the ammonia which evaporated from the bath was provided for by a tube which reached just through the stopper of the Dewar tube, and which, during use, was connected to a suction line. When ready to fill the cell, it was arranged as described above, and the suction turned on. The evaporation of the ammonia under reduced pressure reduced the temperature far below the boiling-point of ammonia under atmospheric pressure. The cylinder of dry ammonia was then attached to the inlet tube of the conductivity cell by means of a rubber tube, which was wound with friction tape for further safety. The manometer was then attached to the exit tube, but with the clamp removed from the manometer, to provide free exit for gases. The ammonia was then turned on, and swept the air out of the cell. Passing through the cooling bath as it does on its way to

the bottom of the cell, the ammonia gas is well cooled before it enters the main cell, and condenses without difficulty. After letting the gas run for a few minutes to clear the air out of the cell, the exit of the gas was shut off by clamping a pinch cock on the rubber tube leading from the manometer. Condensation was so efficient that the mercury in the manometer rarely rose over six inches, which was one fourth the height of the tube. It is safe to say that the pressure never exceeded a third of an atmosphere. If there had been any residual hydrogen, or other non-condensible gas, pressure would have gradually increased. As the distillation proceeded, the heat of condensation of the pure ammonia vaporized the ammonia in the bath; and whenever the ammonia in the bath ran low, the screw clamp closing the tube to the reserve ammonia supply was opened, and the suction refilled the bath.

After something like half filling the cell, the process was stopped, and the manometer removed from the exit tube of t the cell long enough to weigh into the top of the cell the sample of ethyl iodide, and of salt, if one were to be used. These could not be put into the cell first, because the rush of ammonia vapor would carry them out of the cell. Enough ammonia had to be condensed to prevent formation of spray before adding the samples. The manometer was then replaced, and distillation continued until enough ammonia had been condensed to fill the cell to a point on the scale, when

it was stopped, and the cell sealed off. The entrance tube was sealed off first, because it was connected to the bottom of the cell, so that any pressure in the cell with this side open would blow out the ammonia solution. The exit tube was then sealed off, and the cell dipped into ice-water. This proceedure served several purposes. It caused the solution to bump, and thus insured thorough mixing. It brought the temperature of the ammonia in the cell approximately to that of the thermostat; and it served to wash off the ammonia from the cell, which would otherwise lower the freezing point of the water in the thermostat bath, and thus lower its temperature.

The thermostat in which the cell was to be placed was a wooden box, with an inner container consisting of a five-gallon jar insulated from the box by tightly packed sawdust, and secured in place by cement. Drainage was provided for by means of an automatic siphon -- a siphon with both arms of equal length, and both ending with an up-curve. The water level was thus kept at the level of the end of the siphon arm, and the siphon could not empty itself if the water were below this level. The cell itself set in a copper container full of slush ice made from clean ice and distilled water. Experiments showed that this slush-ice remained very closely to zero degrees; the temperature inside the cell itself was never measured.

The cell was removed from the ice-water, and held under

the tap for an instant, to melt off the sheath of ice which always formed when the cell was transferred from the ammonia to the ice-water. It was then set into the copper container of slush-ice in the thermostat. The leads of heavy insulated copper were then brought into the thermostat through glass tubes through holes near the top of the thermostat, and inserted in the mercury wells of the cell. Ice was piled up around the top of the cell as well as was possible without disturbing the electrical connections, the lid closed down, and resistance measurements begun as soon as the rate of change was small enough to permit. During the early part of the run, the middle section of the bridge only was used, but as soon as the change could be followed on the long bridge, it was used.

As the above statements indicate, the measurements vary in degree of accuracy; but fortunately, this variation largely cancels itself out. It is the rate of change of conductance which is really wanted, and this is large when the absolute accuracy of the measurements is poor, and and small when the absolute accuracy is high.

Experience indicated that the cell must stand in the thermostat at least twenty minutes before the measurements are reliable. Because of the fact that the balance obtained when the current was turned on just before the measurements were taken, seemed a little indefinite, the measuring current

was turned on when the lid was closed, hoping to establish equilibrium before measurements were taken.

In order to increase the accuracy of the measurements as far as possible, the readings assigned to particular times do not correspond to single settings of the bridge. Bridge settings were made continuously, perhaps ten in a minute; and the reading asigned to a given time represents the opinion of the experimenter as to its most probable value at that time. It was manifestly i possible to actually average these readings, but it is believed that the method used gave very nearly correct values. They can of course be improved by averaging, and this has been done incalculating.

When the conductance had become practically constant, which was about an hour and a quarter from the time the cell was put into ice-water, the current was turned off and the cell returned to the ammonia bath, and the suction turned on. This quickly reduced the temperature of the ammonia in the cell to a point where it was safe to break of the tip of the exit tube. The solution was then poured out of the cell, never allowed to evaporate, as the salts left on evaporationmight clog up the inlet tube. The cell was then washed out, dried with acetone,the stopcock sealed back on the inlet tube, the exit tube cut off below the constriction, and the cell was ready for another run.

The cell was made with the intention of measuring the volumes of solutions accurately, but an unfortunate oversight on the part of the experimenter rendered the volume readings worthless; and this oversight was not discovered until near the end of the series of experiments. The trouble was simply t that ammonia backed up the inlet tube, filling it up entirely without being noticed.This fact does not in any way invalidate the other data, nor affect the conclusions drawn, but it does make the reduction of conductances to equivalent conductivities impossible.

Although the calibration data was not used, it can do no harm to give it; it at least shows the approximate range of concentrations used. Water was weighed into the cell from a light, specially constructed dropping funnel.

Temperature, 21 degrees.

Original weight of funnel and water, 65.51

Weight funnel	Scale reading	Weight water
32.00	4.50	33.51
31.54	4.08	33.97
30.97	3.50	34.54
30.48	3.04	35.03
29.84	2.45	35.67
29.47	2.10	36.04
28.95	1.54	36.56

The cell constant, defined as the ratio of specific conductance to measured conductance, was determined by mesuring the conductance of an N / 50 solution of KCl, following the directions given in Findlays "Practical Physical Chemistry", page 180, and was found to be 8.425. Although it was thought advisable to determine this constant, no use has ever been made of it.

DATA

Dec. 20, 1920 Wt. C_2H_5I = .5143

TIME	BOX RES.	BRIDGE	CONDUCTANCE	TIME
12:32	1330	5308	Conductances will not be given	
34	1320	4494	for the first part of the data	
35	1040	5055	as they were not used.	
36	1000	5080		
37	940	5031		
38	9000	5021		
39	870	5031		
40	840	5016		
41	810	4992		
42	800	5020		
43	780	5014		
44	750	4970		
45	740	4980		
46	740	5010		

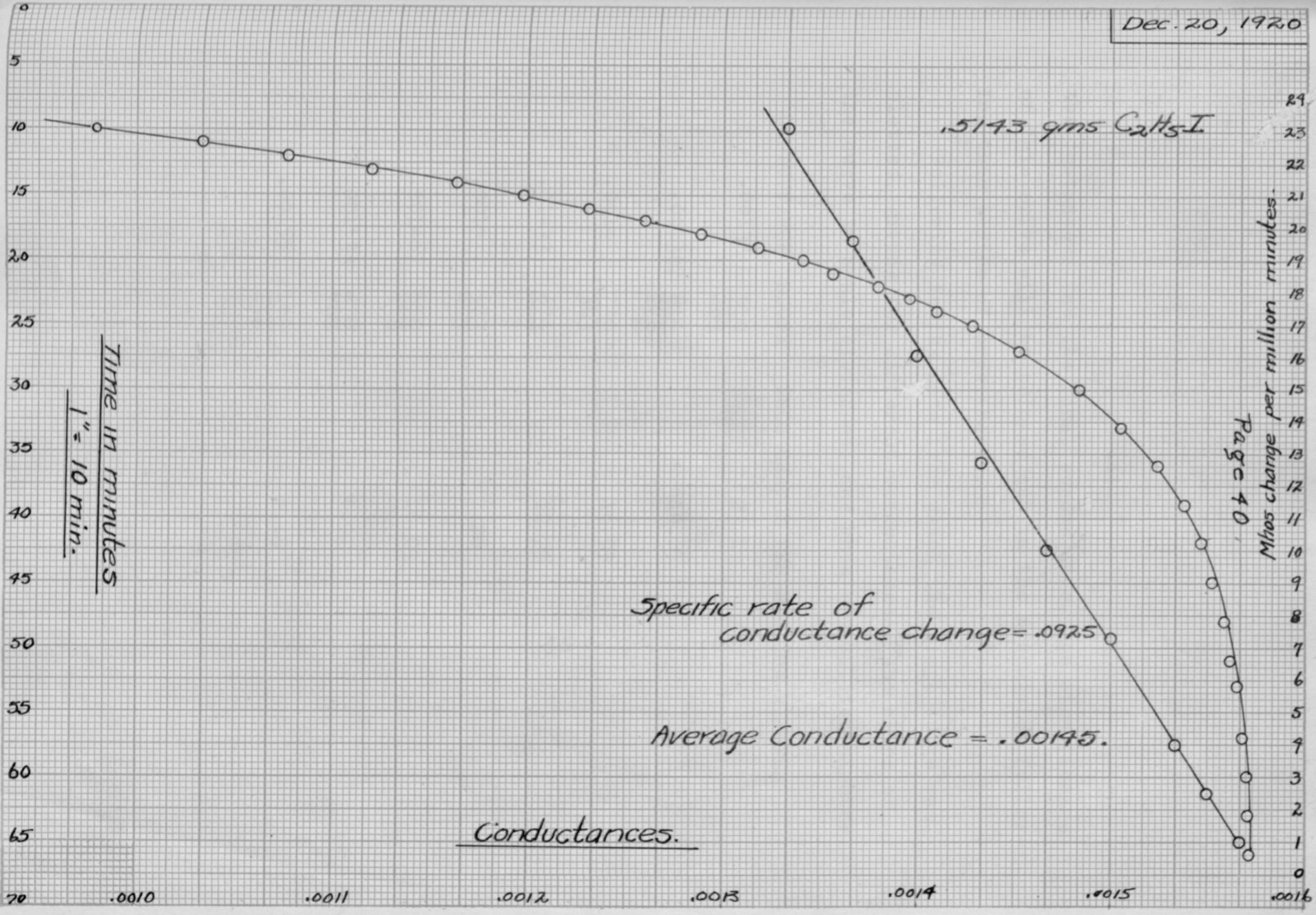
TIME	BOX RES.	BRIDGE	CONDUCTANCE	TIME
12:47	730	5019		
48	720	5014		
49	710	5005		
50	700	5000		
51	690	4990		
52	690	5006	.001453	27
53	685	5003		
54	679	4994		
55	674	5001	.001484	30
56	673	5019		
57	667	4997		
58	664	5000	.001506	33
59	661	5004		
1:00	659	5002		
1	657	5005	.001524	36
2	655	5002		
3	653	5007		
4	651	5000	.001538	39
5	649	5003		

TIME	BOX RES.	BRIDGE	CONDUCTANCE	TIME
1:06	648	5001		
7	647	5004	.001547	42
8	646	5003		
9	644	4997		
10	644	5004	.001552	45
11	643	4997		
12	643	5005		
13	642	5005	.001559	48
14	642	5002		
15	642	5008	.001562	51
16	641	5008		
17	640	5005		
18	639	5001	.001566	53½
19	634	5005		
20	638	4998		
21	638	5000		
22	638	5001	.001568	57
23	638	5001		
24	638	5003		
25	638	5003	.001570	60
26	638	5002		

TIME	BOX RES.	BRIDGE	CONDUCTANCE	TIME
27	638	5005		
28	638	5005	.001571	63
29	638	5006		
30	638	5006		
31	638	5005	.001572	66
32	638	5008		
33	638	5007		
34	638	5006		
35	6387	5007		
41	638	5009		
50	637	5005		
2:00	636	5002		
10	636 5004	5004		
35	635	4997		
3:35	635	4996		
4:45	635	4997		
4:50	636	5001		
5:00	637	5004		

The graphical representation of this data will be found on the following page, along with straight line drawn as the best average value of the rate of change of conductance, plotted against conductance itself; this is equivalent to plotting the rate of change against the difference between

Dec. 20, 1920


.5143 grms C_2H_5I
Time in minutes
1" = 10 min.
Mhos change per million minutes.
Page 40
Specific rate of conductance change = .0925
Average Conductance = .00145.
Conductances.
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
29
23
22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
.0010
.0011
.0012
.0013
.0014
.0015
.0016

the instaneous and the final conductance. The significance of this curve will be pointed out in the discussion following this series of experiments.

Following is the data from which the slope curve was plotted, giving for different conductances, the slope of the curve in scale divisions, and mhos per million minutes.

CONDUCTANCE	SLOPE	MHOS CHANGE PER MILLION MINUTES
.00133	$\frac{910}{263}$	23.1
.001367	$\frac{814}{276}$	19.65
.0014	$\frac{730}{303}$	16.09
.01433	$\frac{674}{352}$	12.75
.0015	$\frac{573}{532}$	7.26
.001467	$\frac{650}{430}$	10.09
.001533	$\frac{478}{796}$	4.01
.00155	$\frac{169}{456}$	2.48

DATA

DEC. 21, 1921

Weight of ethyl iodide = .1510

TIME	BRIDGE	BOX RES.	CONDUCTANCE	TIME
4:35	8000	5274		
36	7000	5182		
37	6000	4983		
38	5000	4700		
39	5000	4840		
39½	5000	4910		
40	5000 4968	4968		
40½	5000	5028		
41	5000	4843	.0002062	11
41½	5000	5122		
42½	4600	5016		
43	4600	5072	.0002224	13
43½	4600	5089		
44	4600	5125		
44½	4600	5144	.0002319	14½
45	4300	5040		
45½	4300	5063		
46	4200	5038	.0002413	16
46½	4200	5056		

TIME	BOX RES.	BRIDGE	CONDUCTANCE	TIME
4:47	4100	5033		
47½	4100	5055	.0002492	17½
48	4080	5064		
48½	4000	5046		
49	4000	5064		
49½	4000	5077	.0002571	19½
50	3900	5030		
50½	3900	5050		
51	3800	5006		
51½	3800	5021		
52	3700	4975	.0002687	22
52½	3700	4978		
53	3700	4992		
53½	3700	5010		
54	3700	5021		
54½	3700	5041	.0002739	24½
55	3630	4991		
55½	3630	5013		
56	3630	5025		
57	3630	5041	.0002800	27
58	3630	5058		

TIME	BOX RES.	BRIDGE	CONDUCTANCE	TIME
4:59	3630	5074		
5:00	3600	5068	.0002861	30½
1	3500	5005		
2	3500	5025		
3	3500	5035		
4	3500	5045		
5	3500	5060	.0002925	35
6	3400	4997		
7	3400	5000		
8	3400	5010		
9	3400	5015		
10	3400	5020	.0002962	39½
11	3380	5008		
13	3340	5000		
14	3340	5000	.0002995	44
15	3340	5005		
17	3330	5005		
19	3330	5006	.0003013	49
21	3330	5012		

TIME	BOX RES.	BRIDGE	CONDUCTANCE	TIME
5:22	3325	5017		
30	3325	5023		
32	3325	5027		
48	3355	5049		
53	3200	4935		
6:00	3200	4935		
07	3680	4493		
7:53	3280	5001		
8:11	3280	5003		
20	3277	5001		
9:30	3277	5003		
11:00	3277	5005		

SLOPE CURVE DATA

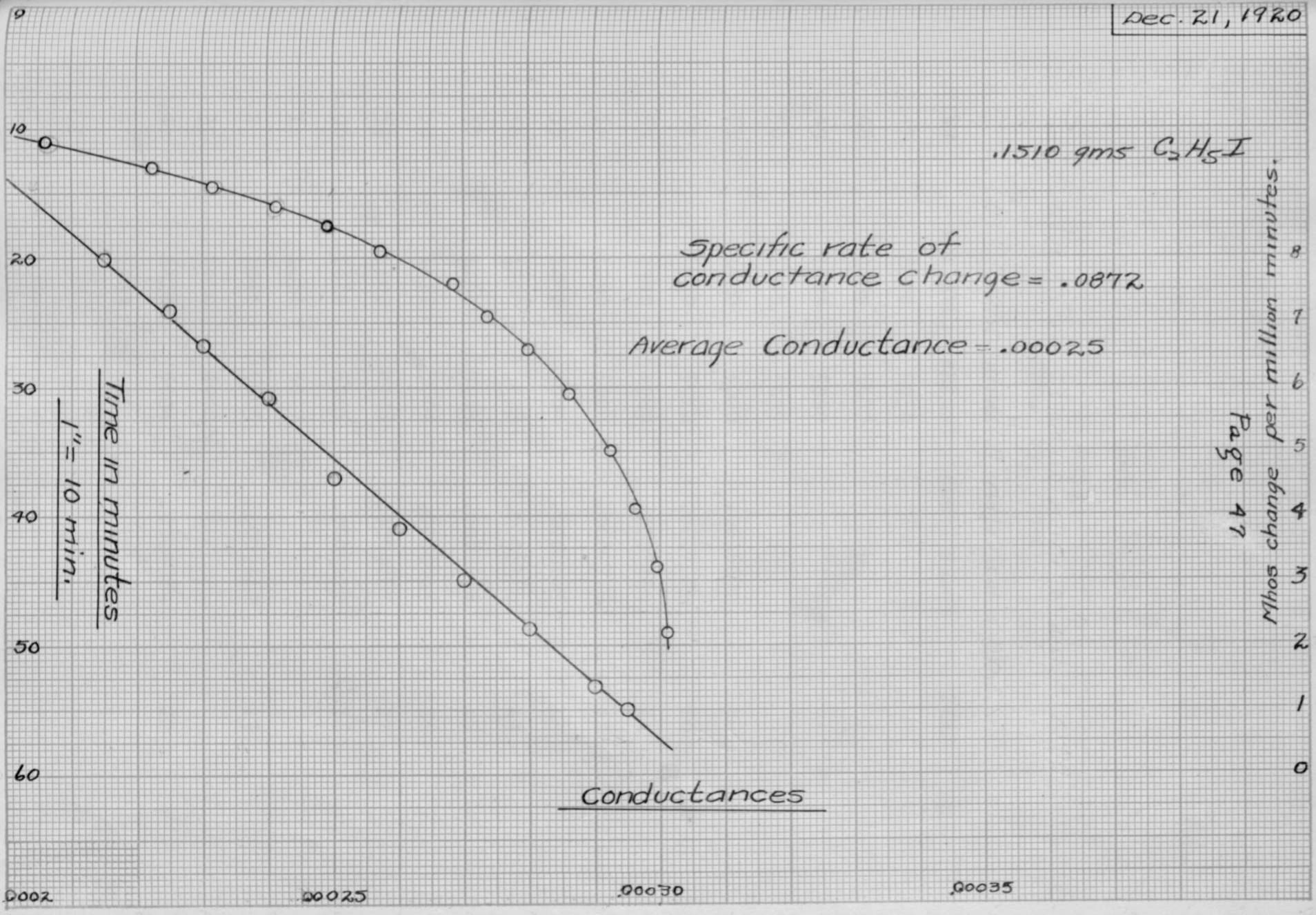
CONDUCTANCE		SLOPE	MHOS CHANGE PER MILLION MINUTES
.000215		$\frac{715}{179}$	7.97
.000225		$\frac{733}{204}$	7.19
.000250		$\frac{7213}{3140}$	4.59
.000260		$\frac{691}{367}$	3.80
.00027	640	$\frac{640}{427}$	3.00
.00028		$\frac{567}{506}$	2.24
.00029		$\frac{44.2}{65.4}$	1.36

CONDUCTANCE	SLOPE MHOS CHANGE PER MILLION MINUTES	
.00029½	$\frac{442}{745}$	1.36
.00024	$\frac{740}{254}$	5.82
.00023	$\frac{7405}{222}$	6.66

This data gives .0872 as the specific rate of conductance change, for an average conductance of .00025 mhos.

Dec. 21, 1920

.1510 gms C_2H_5I



Page 47

DATA

DEC. 29, 1920

.2801 grams of ethyl iodide used.

TIME	BOX RES.	BRIDGE	CONDUCTANCE	TIME
3:47	2200	5050		
48	2000	5037		
49	1800	5060		
50	1640	5035		
51	1520	5020	.0006632	9
52	1430	5012	.0007026	10
53	1340	4989	.0007430	11
54	1290	5008	.0007778	12
55	1240	5004	.0008085	13
56	1200	5008	.0008386	14
57	1160	5005	.0008636	15
58	1130	5004	.0008865	16
59	1100	4998	.0009087	17
4:00	1080	5005	.0009277	18
1	1060	5007		
2	1040	5005	.0009462	19
3	1020	4992		
4	1010	5004	.0009889	22
5	1003	5021		

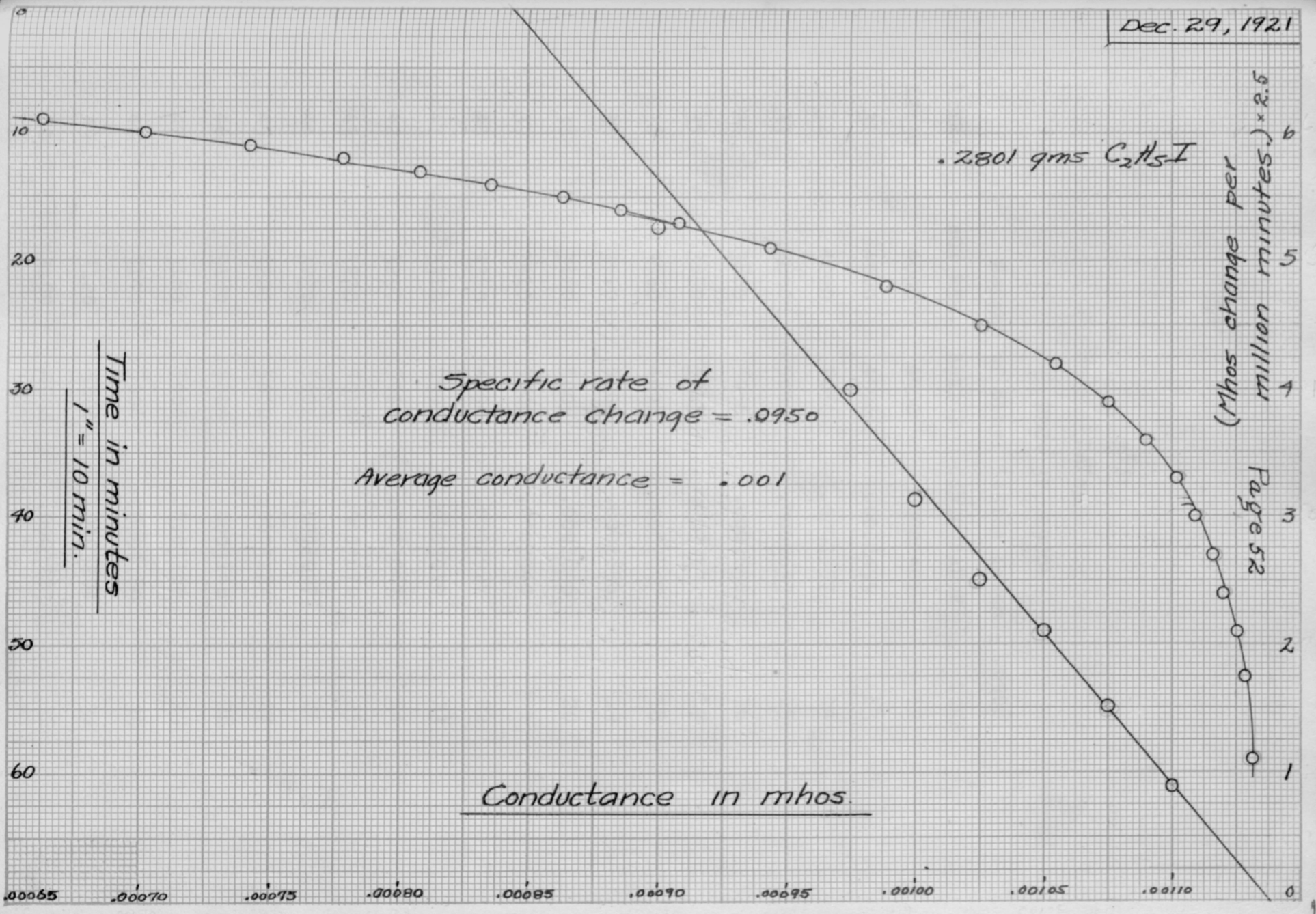
TIME	BOX RES.	BRIDGE	CONDUCTANCE	TIME
6	990	5016		
7	974	5004	.001028	25
8	964	5001		
9	955	4999		
10	947	5000	.001055	28
11	941	4998		
12	936	5000		
13	930	5000	.001075	31
14	925	4999		
15	921	4999		
16	918	5002	.0010901	34
17	914	5001		
18	910	5000		
19	907	5000	.0011022	37
20	905	5000		
21	903	4999		
22	900	4997	.0011097	40
23	899	5000		

TIME	BOX RES.	BRIDGE	CONDUCTANCE	TIME
4:24	897	5002		
25	896	5004	.0011168	43
26	894	49975	.	
27	893	5002		
28	892	5001	.0011215	46
29	890	49985		
30	889	49985		
31	888	4998	.0011253	49
32	888	5002		
33	887	5005		
34	886	5000	.0011292	52½
35	885	4998		
36	885	5000		
37	885	5002		
38	885	5003	.0011315	56½
39	884	5001		
40	884	50025		
48	881	5000		
5:15	880	5003		
50	880	5002		
Next A.M.	880	4990		

SLOPE CURVE DATA

CONDUCTANCE	SLOPE	(MHOS PER MILLION MINUTES) × 2.5
$90 \cdot 10^{-4}$	$\frac{852}{212}$	5.25
97.5	$\frac{990}{310}$	4.00
100	$\frac{830}{332}$	3.12
102.5	$\frac{709}{345}$	2.50
105	$\frac{889}{529}$	2.10
$107\frac{1}{2}$	$\frac{707}{588}$	1.50
110	$\frac{475}{669}$	.88
$112\frac{1}{2}$	$\frac{198}{77}$	.32

The specific rate of conductivity change as given by this data is .0950, for an average conductance of .001


.2801 gms C_2H_5I
Specific rate of conductance change = .0950
Average conductance = .001
Time in minutes
1" = 10 min.
Conductance in mhos
(Mhos change per second) × 2.5 millionths
Page 52
10
20
30
40
50
60
.00065
.00070
.00075
.00080
.00085
.00090
.00095
.00100
.00105
.00110
0
1
2
3
4
5
6

DATA

DEC. 30, 1920

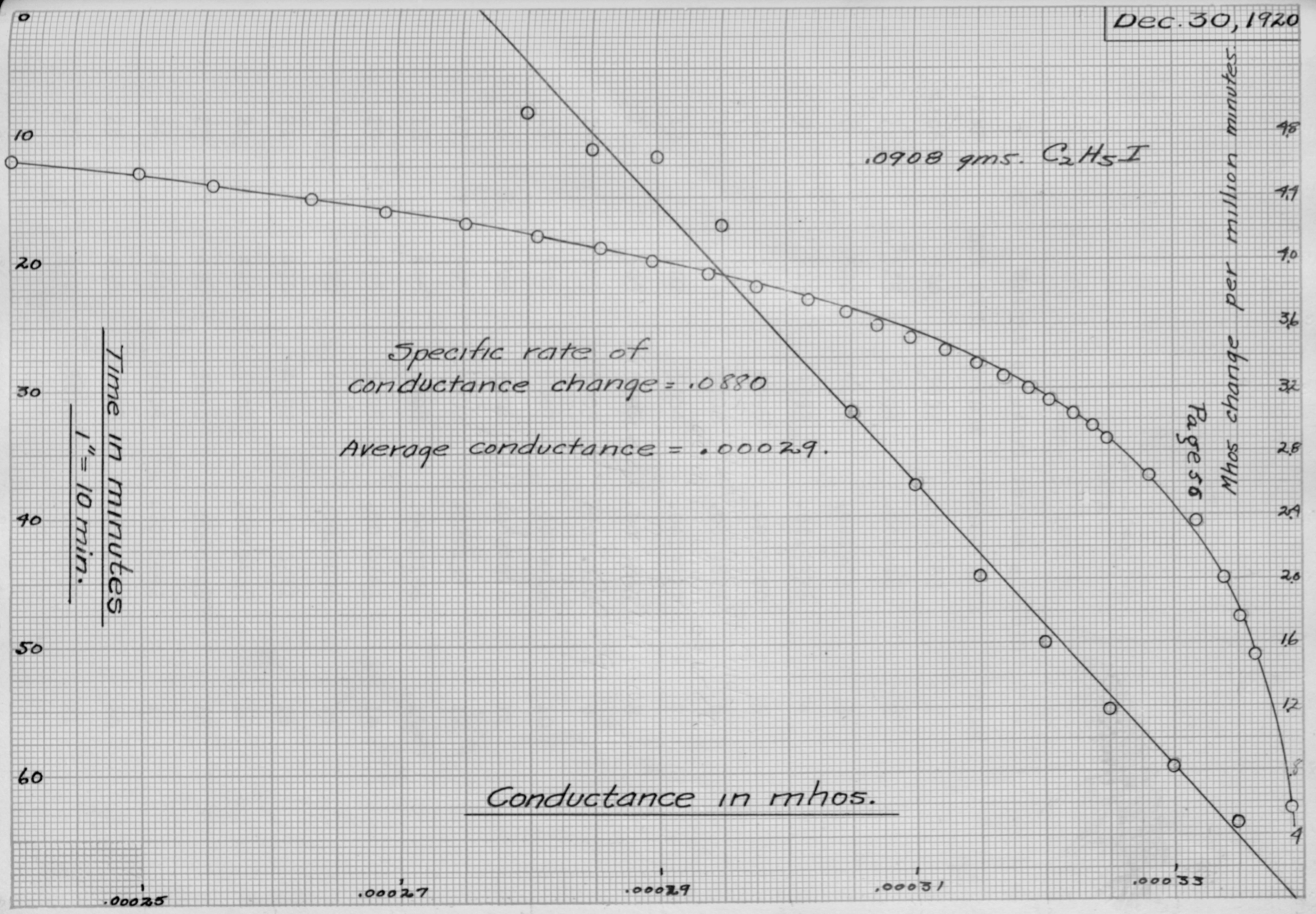
Weight of ethyl iodide taken = .0908

TIME	BOX RES.	BRIDGE	CONDUCTANCE	TIME
12:30	4000	4900	.0002401	12
31	4000	4996	.0002499	13
32	4000	5056	.0002557	14
33	3800	5002	.0002633	15
24	3800	5056	.0002690	16
35	3650	5013	0002753	17
36	3560	4998	.0002807	18
37	3510	5006	.0002856	19
38	3460	5005	.0002896	20
39	3410	5006	.0002940	21
40	3350	4994	.0002977	22
41	3310	2998	.0003019	23
42	3290	5006	.0003047	24
43	3270	5010	.0003070	25
44	3230	5001	.0003097	26
45	3200	5000	.0003124	27
46	3180	5004	.0003148	28
47	3160	5004	.0003169	29
48	3140	5004	.0003189	30
49	3120	5000	.0003204	31
50	3100	4998	.0003223	32

TIME	BOX RES.	BRIDGE	CONDUCTANCE	TIME
12:51	3080	4994	.0003239	33
52	3060	4985	.0003249	34
54	3060	5004		
55	3050	5006	.0003283	37
56	3040	5000		
57	3030	5004		
59	3030	5016		
1:00	3010	4998	.0003319	41½
1	3000	4997		
2	2990	4994		
3	2990	4997	.0003340	45
4	2990	5000		
5	2990	5005		
6	2980	5000	.0003351	48
7	2980	5005		
8	2980	5007		
9	2970	5000	.0003364	51
10	2970	4997		
17	2960	5004		
19	2960	2951	.0003386	60
20	2960	5007		

SLOPE CURVE DATA

CONDUCTANCE	SLOPE	MHOS CHANGE PER MILLION MINUTES
29	$\frac{106}{228}$	4.65
29½	$\frac{101.1}{24.2}$	4.18
30	$\frac{959}{252}$	3.81
30½	$\frac{857}{272}$	3.15
31	$\frac{743}{287}$	2.59
31½	$\frac{911}{452}$	2.02
32	$\frac{797}{497}$	1.60
32½	$\frac{649}{550}$	1.18
33	$\frac{500}{605}$	.826
33½	$\frac{305}{641}$	.474
28½	$\frac{1062}{2260}$	4.70
28	$\frac{108}{219}$	4.93


Dec. 30, 1920
.0908 gms. C_2H_5I
Specific rate of conductance change = .0880
Average conductance = .000279.
Page 56
Mhos change per million minutes
Time in minutes
1" = 10 min.
Conductance in mhos.
0
10
20
30
40
50
60
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
.8
.4
.000125
.000127
.000129
.000131
.000133

DATA

Jan. 3, 1921

Weight of ethyl iodide = .5830

TIME	BOX RES.	BRIDGE	CONDUCTANCE	TIME
4:06	530	5002	.001888	1
7	525	5004	.001908	2
8	520	5000	.0019231	3
9	515	4993	.0019376	4
10	512	4995	.0019500	5
11	510	5002	.0019625	6
12	507	5004	.0019727	7
13	505	5005	.0019843	8
14	503	5005	.00i9920	9
15	501	5007	.0020016	10
16	500	5008	.0020016	11
17	495	4992	0020137	12
18	495	4998	.0020186	13
19	495	5005	.0020243	14
20	490	4986	.0020296	15
21	490	4992	.0020342	16
22	490	5000	.0020408	18
23	490	5000	.0020408	18
24	490	5004	.0020442	19
25	490	5008	.0020475	20
26	490	5010	,0020492	21

TIME	BOX RES.	BRIDGE	CONDUCTANCE	TIME
4:27	490	5014	.0020521	22
28	485	4991	.0020546	23
29	485	4994		
30	485	4996	.0020576	24½
31	485	4999		
32	485	5000	.0020614	26½
33	485	5000		
34	485	50025	.0020624	28½
35	485	50048		
36	485	50053	.0020661	30½
37	485	50060		
38	485	50065	.0020670	32½
39	485	50080		
40	485	50085	.0020687	35
41	485	50089		
42	485	50100	.00	
43	485	50108	.0020708	38
44	485	50113		

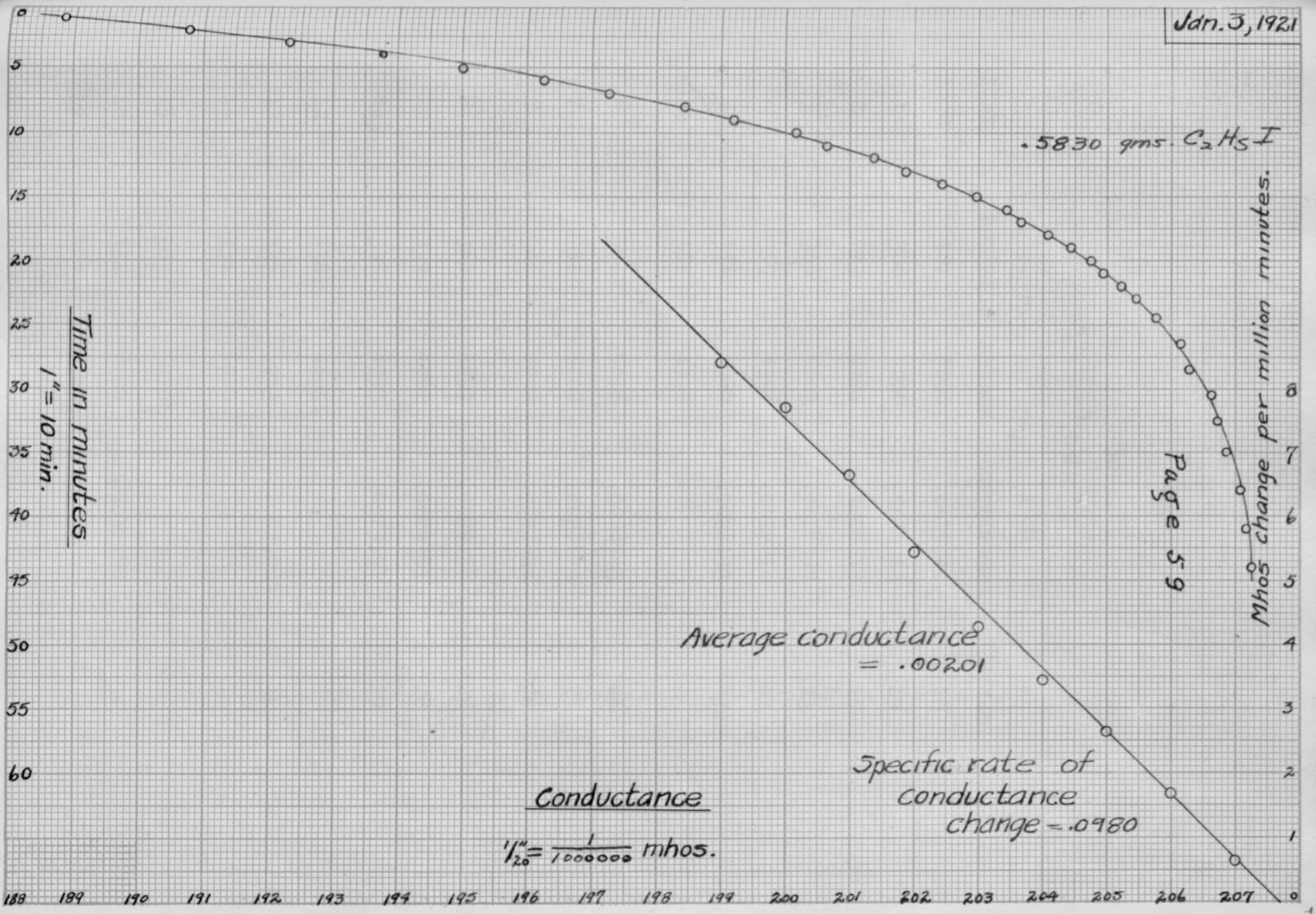
TIME	BOX RES.	BRIDGE	CONDUCTANCE	TIME
4:45	485	50120		
46	485	50120	.0020717	41
47	485	50123		
48	485	50130		
49	485	50133	.0020725	44
50	485	50131		

SLOPE CURVE DATA

CONDUCTANCE	SLOPE	MHOS CHANGE PER MILLION MINUTES
.00199	$\frac{822}{195.2}$	8.42
.00200	$\frac{582}{151}$	7.71
.00201	$\frac{525}{1583}$	6.64
.00202	$\frac{740}{272}$	5.44
.00203	$\frac{640}{298}$	4.28
.00204	$\frac{540}{313}$	3.44
.00205	$\frac{421}{321}$	2.63
.00206	$\frac{370}{438}$	1.69

Specific rate of conductance change = .0980

Average conductance = .00201


Jan. 3, 1921
.5830 gms. C_2H_5I
Page 59
Mhos change per million minutes.
Average conductance = .00201
Specific rate of conductance change = .0980
Conductance
1/20" = 1/1000000 mhos.
Time in minutes
1" = 10 min.
0
5
10
15
20
25
30
35
40
45
50
55
60
8
7
6
5
4
3
2
1
0
188
189
190
191
192
193
194
195
196
197
198
199
200
201
202
203
204
205
206
207

DATA

Jan. 5, 1921

TIME	BOX RES.	BRIDGE	CONDUCTANCE	TIME
3:00	387	5000	.0025840	18
1	380	5000	.0026316	19
2	273	5000	.0026810	20
3	366	5003	.0027377	21
4	359	4996	.0027810	22
5	354	4980	.0028133	23¼
5½	354	4996		
6	354	5018	.0028543	24½
7	350	5009	.0028674	25
8	346	5002	.0028926	26
9	342	4993	.0029158	27
10	339	4991	.0029393	28
11	337	4993	.0029591	29
12	336	4995		
13	335	5003	..0029883	31
14	334	5010		
15	383	5010		
16	331	5006	.0030280	34
17	329	5000		

TIME	BOX RES.	BRIDGE	CONDUCTANCE	TIME
3:18	328	4998		
19	328	5004	.0030543	37
20	327	5004		
21	326	5001		
22	325	4998	.0030716	39½
23	325	5002		
24	324	4999	.0030853	42
25	324	5004		
26½	323	4999		
27	323	5000	.0030960	44¾
28	322	4966		
29	322	4997	.0031019	46½
29½	322	4997		
30	322	4999	.0031044	48
30½	322	4999		
31	322	5002		
31½	322	5002	.0031081	49½
32	322	5003		

TIME	BOX RES.	BRIDGE	CONDUCTANCE	TIME
3:33	322	5007		
33½	322	5005	.0031131	51½
34	322	5006		
34¼	322	5006		
35	321	5000	.0031165	53¼
35½	321	5002		
36½	321	5003		
37	321	5003	.0031190	55
37½	321	5003		
39	321	5002		
40	321	5004	.0031203	58
41	321	5005		
42	321	5005		
43	321	5004	.0031215	61
44	321	5007		
45	321	5007		
46	321	5007	.0031240	64
47	321	5008		

SLOPE CURVE DATA

CONDUCTANCE	SLOPE	MHOS CHANGE PER MILLION MINUTES
.00290	830 / 170	24.5
.00295	769 / 199	19.25
.00300	640 / 249	12.8
.003025	576 / 269	8.05
.00305	768 / 477	805
.003075	641 / 568	5.64
.00310	475 / 723	3.28
.0031125	350 / 910	1.93

Specific rate of conductivity change = .1065

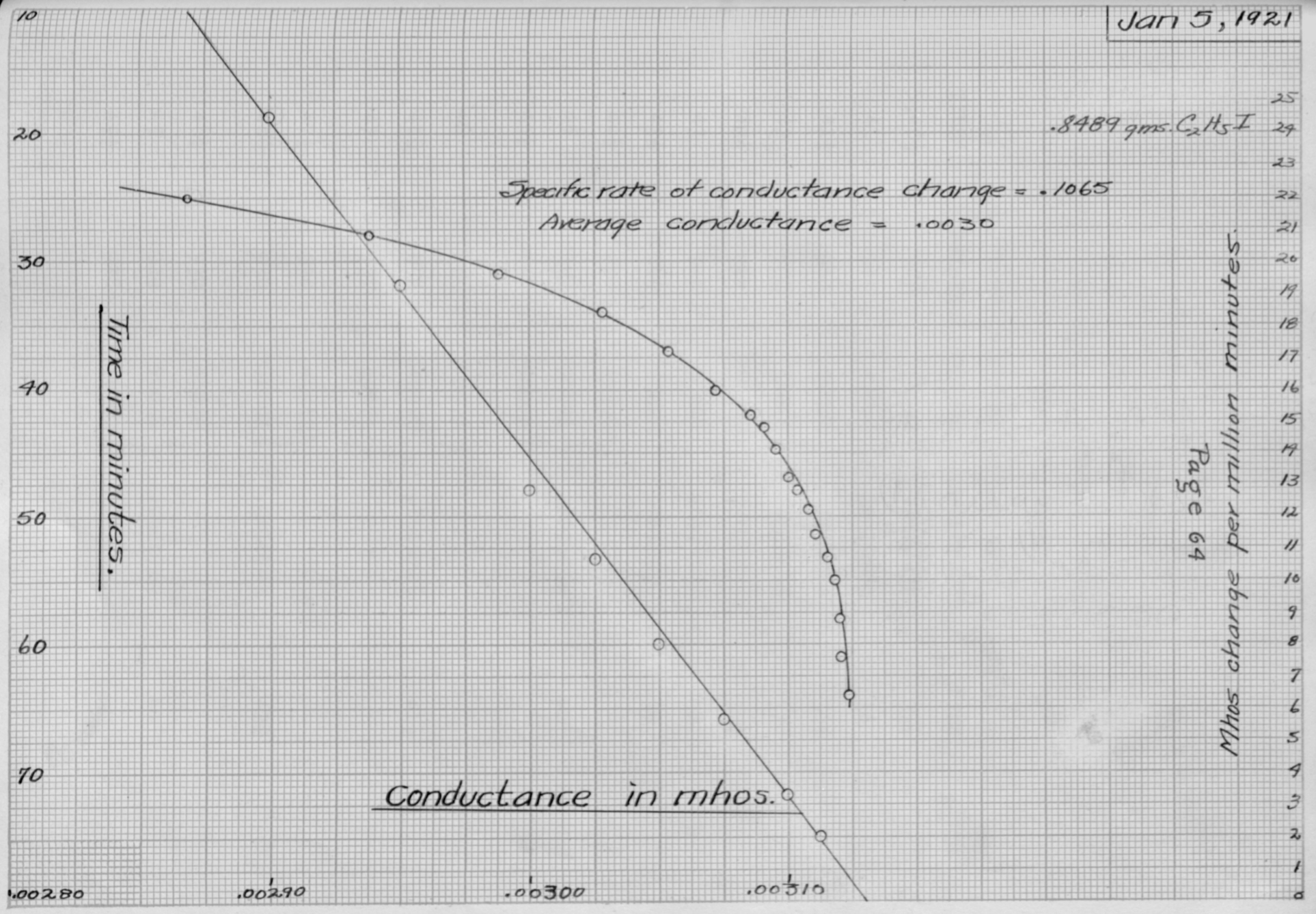
Average conductance =-.0030

Jan 5, 1921

.8489 gms. C_2H_5I

Specific rate of conductance change = .1065

Average conductance = .0030



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DATA

Jan. 12, 1921

Weight of ethyl iodide used = .2663

TIME	BOX RES.	BRIDGE	CONDUCTANCE	TIME
5:40½	946	50012	.0010575	35½
41	944	49990	.0010589	36
41½	943	50005	.0010604	36½
42	942	50010	.0010620	37
42½	941	50015	.0010631	37½
43	940	50022	.0010647	38
43½	940	50022	.001661	39
44½	936	49998		
45	935	50002	.0010696	40
45½	934	50000		
46	933	50000		
46½	932	49998	.0010728	41½
47	931	49992		
47½	930	49982		
48	930	50002	.0010748	42¾
48½	930	50020		
49	929	50010	.0010769	44
49½	928	50002		

TIME	BOX RES.	BRIDGE	CONDUCTANCE	TIME
5:50½	926	49985		
51	926	49995	.0010776	46
51½	926	50009		
52	925	50002		
52½	925	50012	.0010814	47¼
53	925	50023		
53½	924	50012		
53	925	50023	.0010824	48¼
54	923	49992		
54½	923	50004	.0010835	49½
55	923	50014		
55½	922	49997		
56	922	50009	.0010847	50¾
56½	921	49990		
57	921	49995	.10857	52
57½	921	50008		
58	920	49986		
58½	920	49994	.0010866	53¼

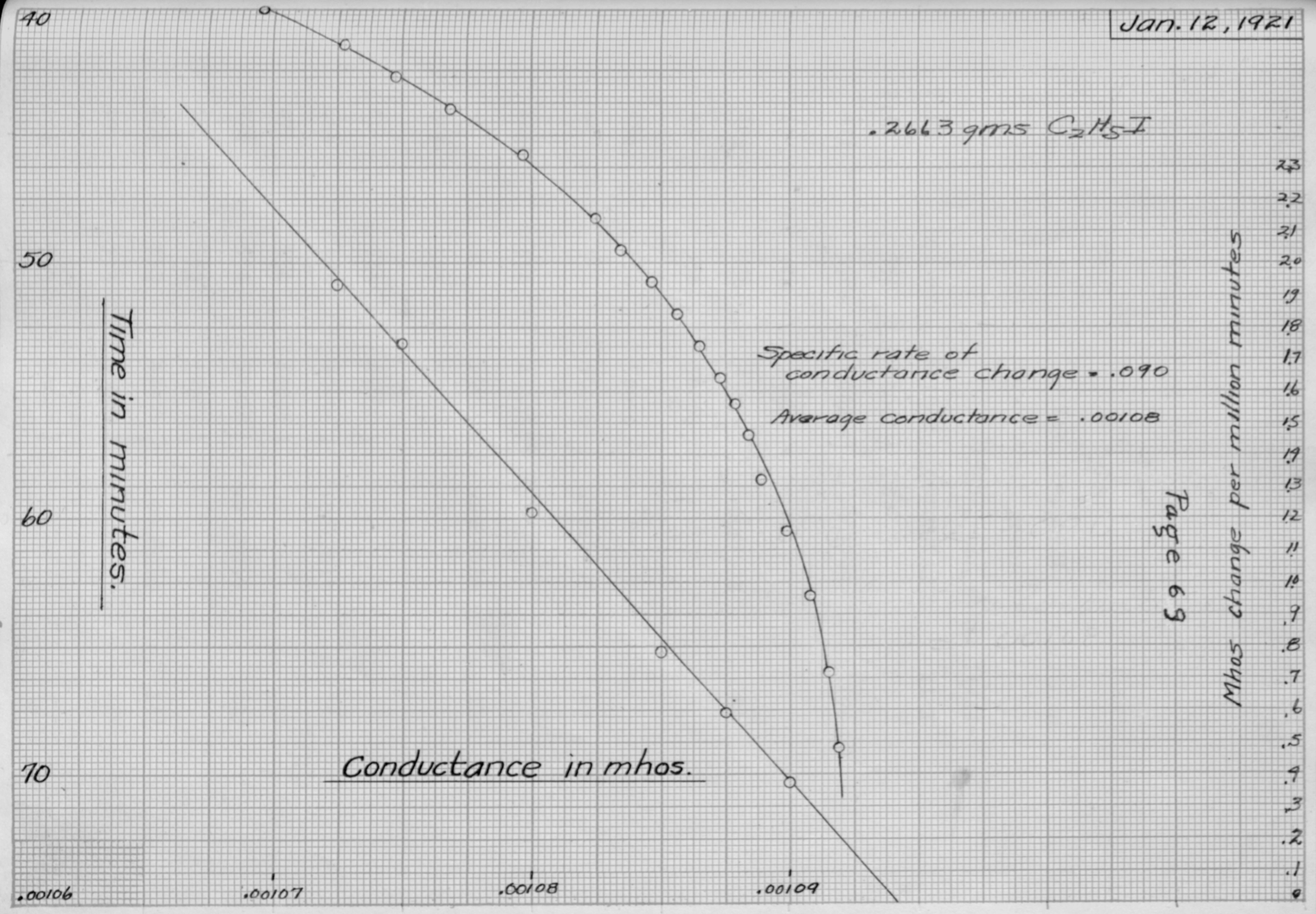
TIME	BOX RES.	BRIDGE	CONDUCTANCE	TIME
5:59	920	50000		
59½	920	50006	.0010873	54½
6:00	920	50015		
½	919	49993		
1	919	49998	.0010879	55¾
1½	919	50006		
2	919	50010	.0010884	56¾
3	918	49994		
4	918	50002	.0010892	58½
5	918	50010		
6	918	50016	.0010899	60½
7	916	49972		
8	916	49981	.0010908	63
9	916	49985		
6:10	916	49995		
11	916	49995	.0010916	66
12	916	50000		
13	916	50003		
14	916	50005	.0010919	69
15	916	50010		

SLOPE CURVE DATA

CONDUCTANCE	SLOPE	MHOS CHANGE PER MILLION MINUTES
.0010725	$\frac{721}{376}$	1.933
.0010750	$\frac{743}{425}$	1.750
.0010800	$\frac{746}{603}$	1.218
.0010825	$\frac{737}{727}$	1.618
.0010850	$\frac{694}{883}$	.785
.0010875	$\frac{635}{1078}$	.589
.0010900	$\frac{229}{610}$	.376
.0010912	$\frac{103}{200}$	.052

Jan. 12, 1921

.2663 gms C_2H_5I



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DATA

Feb. 14, 1921

.2515 grams KI

.1590 grams ethyl iodide

TIME	BOX RES.	BRIDGE	CONDUCTANCE	TIME
2:41	558	50000		
41½	558	50025	.001793	7¼
42	556	49965		
42½	556	49990	.0017974	8¼
43	556	50000		
43½	556	50010		
44	556	50028	.0017996	9¾
44½	555	49996		
45	555	50010	.0018024	11
45½	555	50023		
46	554	49990		
46½	554	49996	.0018049	12½
47	554	50005		
47½	554	50020	.0018059	13¼
48	553	49989		
48½	553	49995	.0018080	14½
49	553	50004		
49½	553	50010		

TIME	BOX RES.	BRIDGE	CONDUCTANCE	TIME
2:50	553	50018	.0018097	16
50½	555	50030		
51	552	49995		
51½	552	50002	.0018115	17½
52	552	5006		
52½	552	50015		
53	552	50025	.0018132	19
53½	552	50031		
54	551	49993		
54½	551	4998	.0018149	20½
55	551	50005		
55½	551	50008		
56	551	50014		
56½	551	50026	.0018166	22¼
57	551	50030		
57½	550	50090		
58	550	50092	.0018172	24
58½	550	50093		
59	550	50098		
59½	550	50002	.0018181	25¼

TIME	BOX RES.	BRIDGE	CONDUCTANCE	TIME
3:00	550	50004		
½	550	50010	.0018186	26¼
1	550	50013		
1½	550	50015	.0018192	27½
2	550	50018		
2½	550	50020		
3	550	50027	.0018198	29
3½	550	50025		
4	550	50026		
5	550	50030	.0018203	31
6	550	50033		
7	549	49997		
8	549	50000	.0018214	34
9	549	50004		
10	549	50005		
11	549	50008	.0018220	37
12	549	50009		
13	549	50007		
14	549	50010	.0018222	40
15	549	50010		

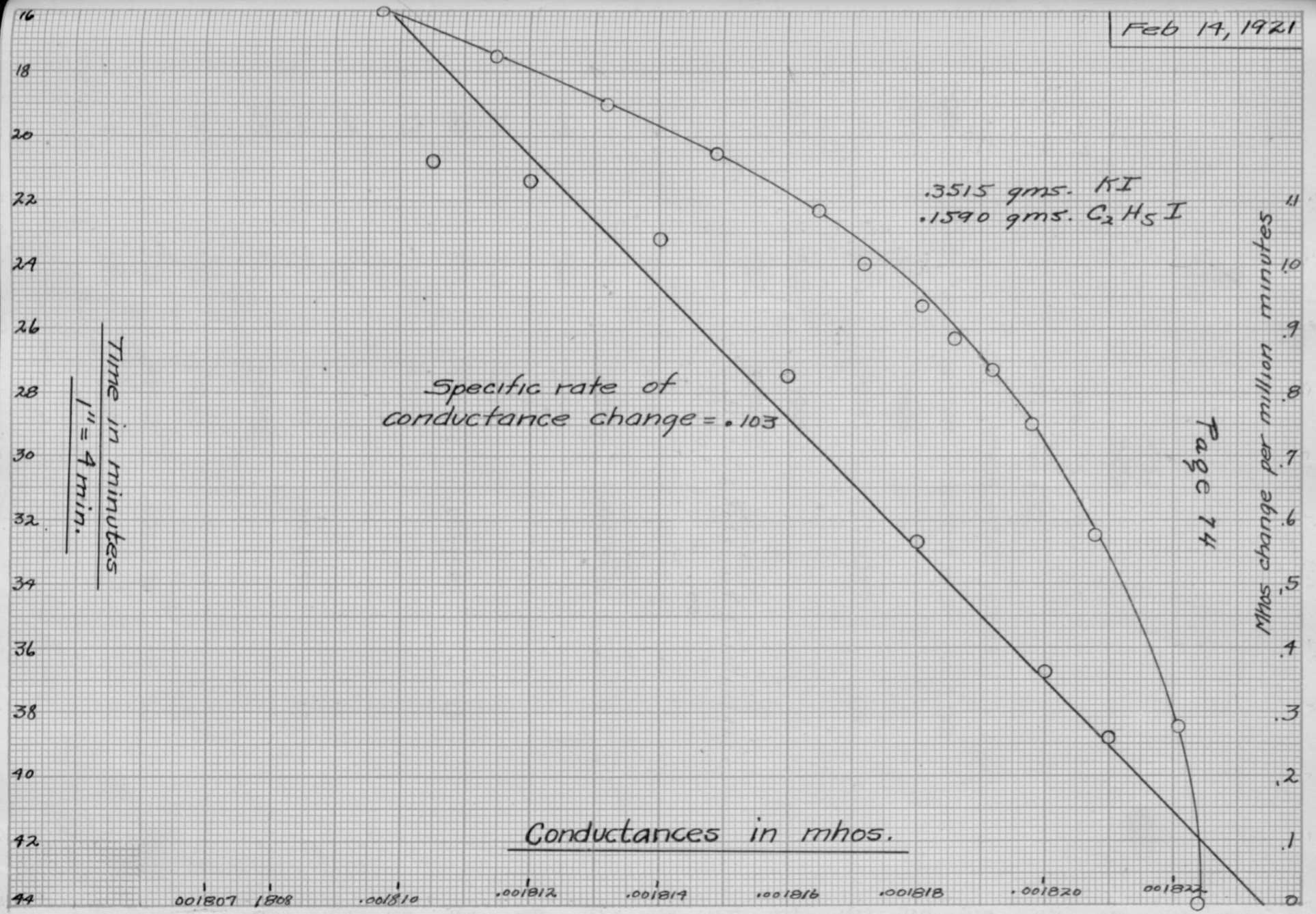
TIME	BOX RES.	BRIDGE	CONDUCTANCE	TIME
3:16	549	50012		
16	549	50015	.0018224	44
20	549	50021		
22	549	50019		
24	549	50020	.0018229	50
26	549	50021		

SLOPE CURVE DATA

CONDUCTANCE	SLOPE	MHOS CHANGE PER MILLION MINUTES
.0018105	$\frac{700}{305}$	1.160
.001812	$\frac{701}{310}$	1.130
.001814	$\frac{691}{333}$	1.039
.001816	$\frac{677}{378}$	.826
.001818	$\frac{790}{702}$	.564
.001820	$\frac{565}{919}$	.361
.001821	$\frac{49}{95}$	.258

Specific rate of conductance change = .103

Average conductance = .00182


.3515 gms. KI
.1590 gms. C_2H_5I
Specific rate of conductance change = .103
Time in minutes
1" = 4 min.
Mhos change per million minutes
Conductances in mhos.
16
18
20
22
24
26
28
30
32
34
36
38
40
42
44
11
10
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
.001807
.1808
.001810
.001812
.001814
.001816
.001818
.001820
.001822

DATA

Feb. 15, 1921

.4070 grams KI

.1312 grams ethyl iodide

TIME	BOX RES.	BRIDGE	CONDUCTANCE	TIME
4:03	521	50024		
4	520	50045	.0019235	3½
5	518	49990		
6	518	50041	.0019330	6
7	516	49990		
8	515	49985		
9	515	50016	.0019431	9
10	514	50004		
11	513	49984		
12	513	50014	.0019505	12
13	512	49980		
14	512	50028		
16	511	50003	.0019555	15
15	512	50028		
17	511	50020		
18	510	49982	.0019596	18
19	510	49995		

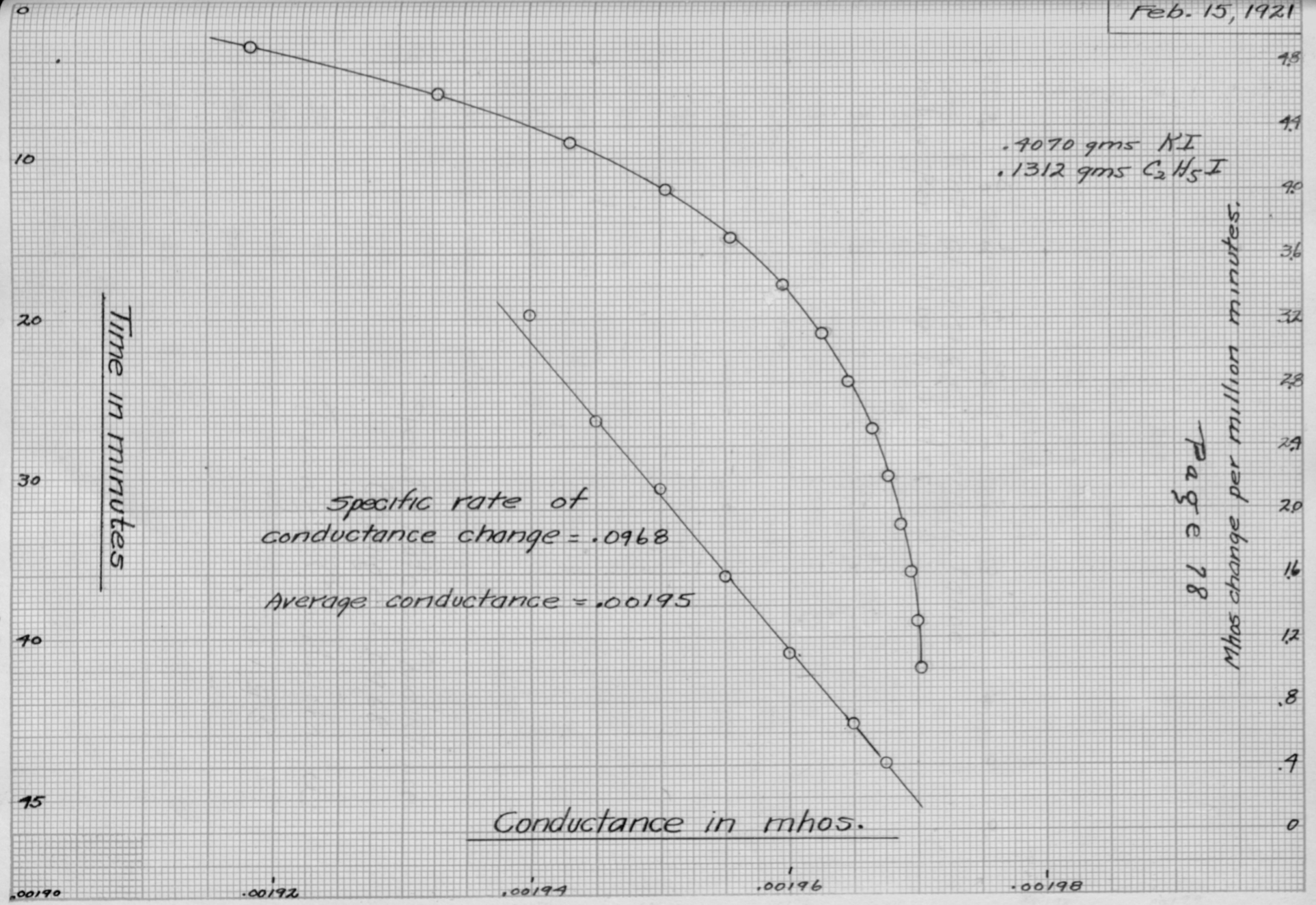
TIME	BOX RES.	BRIDGE	CONDUCTANCE	TIME
4:20	510	50008		
21	510	50021	.0019626	21
22	509	49983		
23	509	49992		
24	509	5002	.0019648	24
25	509	50010		
26	509	50019		
27	509	50022	.0019665	27
28	508	49980		
29	508	49984	.	
30	508	49990	.0019677	30
31	508	49998		
33	508	5004		
34	508	5007	.0019687	33
32	508	49998		
35	508	50008		
35	508	50015	.0019695	36
37	508	50015		
38	508	50017		
39	508	50018	.0019700	39
40	508	50022		

TIME	BOX RES.	BRIDGE	CONDUCTANCE	TIME
4:41	508	50020		
42	508	50024	.0019703	42
43	508	50024		

SLOPE CURVE DATA

CONDUCTANCE	SLOPE	MHOS CHANGE PERMILLION MINUTES
.00194	$\frac{656}{254}$	3.230
.1945	$\frac{590}{288}$	2.560
.00195	$\frac{531}{312}$	2.130
001955	$\frac{752}{590}$	1.591
.00196	$\frac{751}{861}$	1.008
.001965	$\frac{409}{777}$	.660
.0019675	$\frac{256}{787}$	.41

Feb. 15, 1921


.4070 gms KI
.1312 gms C_2H_5I
Specific rate of
conductance change = .0968
Average conductance = .00195
Time in minutes
Conductance in mhos.
Mhos change per million minutes.
0
10
20
30
40
45
.00190
.00192
.00194
.00196
.00198
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
.8
.4
0

DATA

Feb 16, 1921

.1911 grams KNO_3

.1150 grams C_2H_5I

TIME	BOX RES.	BRIDGE	CONDUCTANCE	TIME
3:36	970	50075	.001034	6
37	966	50040	.001036	7
38	962	50005	.001039	8
39	960	50025	.001043	9
40	958	50030	.001045	10
41	955	50000	.001047	11
42	954	50015	.001049	12
43	952	50010		
44	950	49985	.0010519	14
45	949	49997		
46	948	50002		
48	946	50000	.0010567	18
49	945	50000		
50	944	49995		
51	943	49995	.0010600	21
52	942	49982		
53	941	49970		
54	941	50000	.0010619	24
55	941	49980		

DATA

TIME	BOX RES.	BRIDGE	CONDUCTANCE	TIME
3:56	941	50015		
58	941	50033	.0010640	28
59	940	50020		
60	940	50027		
4:01	939	50005	.0010652	31
2	939	50007		
3	939	50014		
4	939	50020	.0010658	34
5	939	50025		
6	938	499995		
7	938	50008	.0010661	37
8	938	50013		
9	938	50017		
10	938	50019	.0010666	40
11	938	50018		
12	938	50020		
13	938	50023	.001069	43
14	938	50026		
15	938	50028		
16	938	50034	.001073	46

TIME	BOX RES.	BRIDGE	CONDUNTANCE	TIME
4:17	938	50037		
18	936	50099		
19	936	50083		
20	936	50087	.0010677	50
21	936	50088		
22	936	50086		

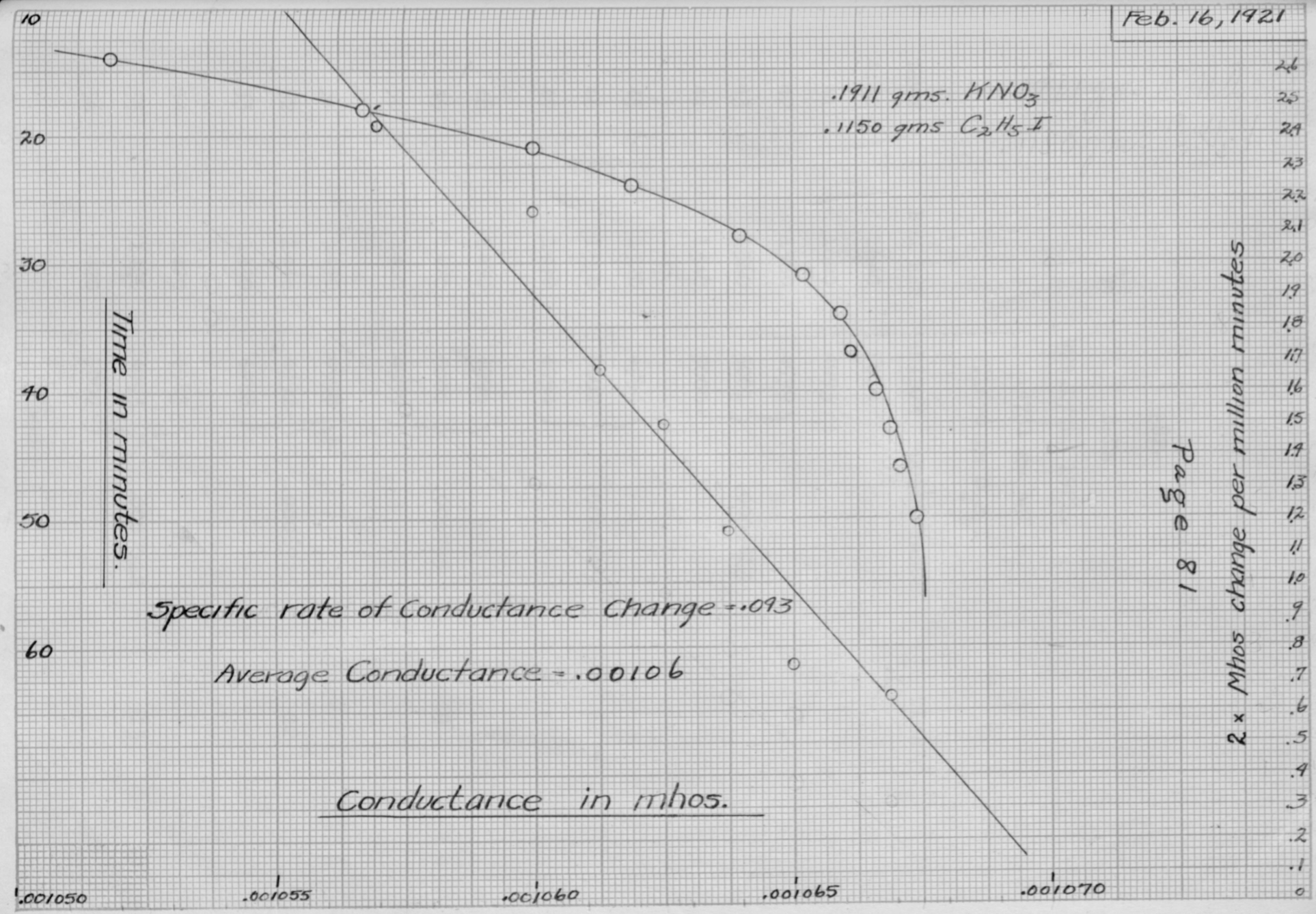
SLOPE CURVE DATA

CONDUCTANCE	SLOPE	MHOS CHANGE PER MILLION MINUTES
.0010525	$\frac{710}{169}$	1.31
.0016000	$\frac{631}{182}$	1.08
.0016120	$\frac{822}{308}$	.835
.0016250	$\frac{773}{323}$	.747
.0016375	$\frac{652}{351}$	.580
.0016500	$\frac{770}{649}$	.375
.0016680	$\frac{225}{633}$	.111

AVERAGE CONDUCTANCE = .00106

SPECIFIC RATE OF CONDUCTANCE CHANGE = .093

Feb. 16, 1921



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DATA

FEB.17th, 1921.

.4731 gm AgI

.1670 gm C_2H_5I

TIME	BOX RES.	BRIDGE	CONDUCTANCE	TIME
4:40	1640	5014		
41	1600	4993		
42	1580	4999		
43	1560	5001	.0006413	3
44	1540	5000		
45	1520	4994		
46	1510	5002	.0006629	6
47	1490	4994		
48	1480	4996		
49	1470	5000	.006795	9
50	1460	4999		
51	1450	4998		
52	1440	4992	.0006925	12
53	1430	4988		
54	1420	4983		
55	1420	4993	.0007022	15
56	1420	5002		

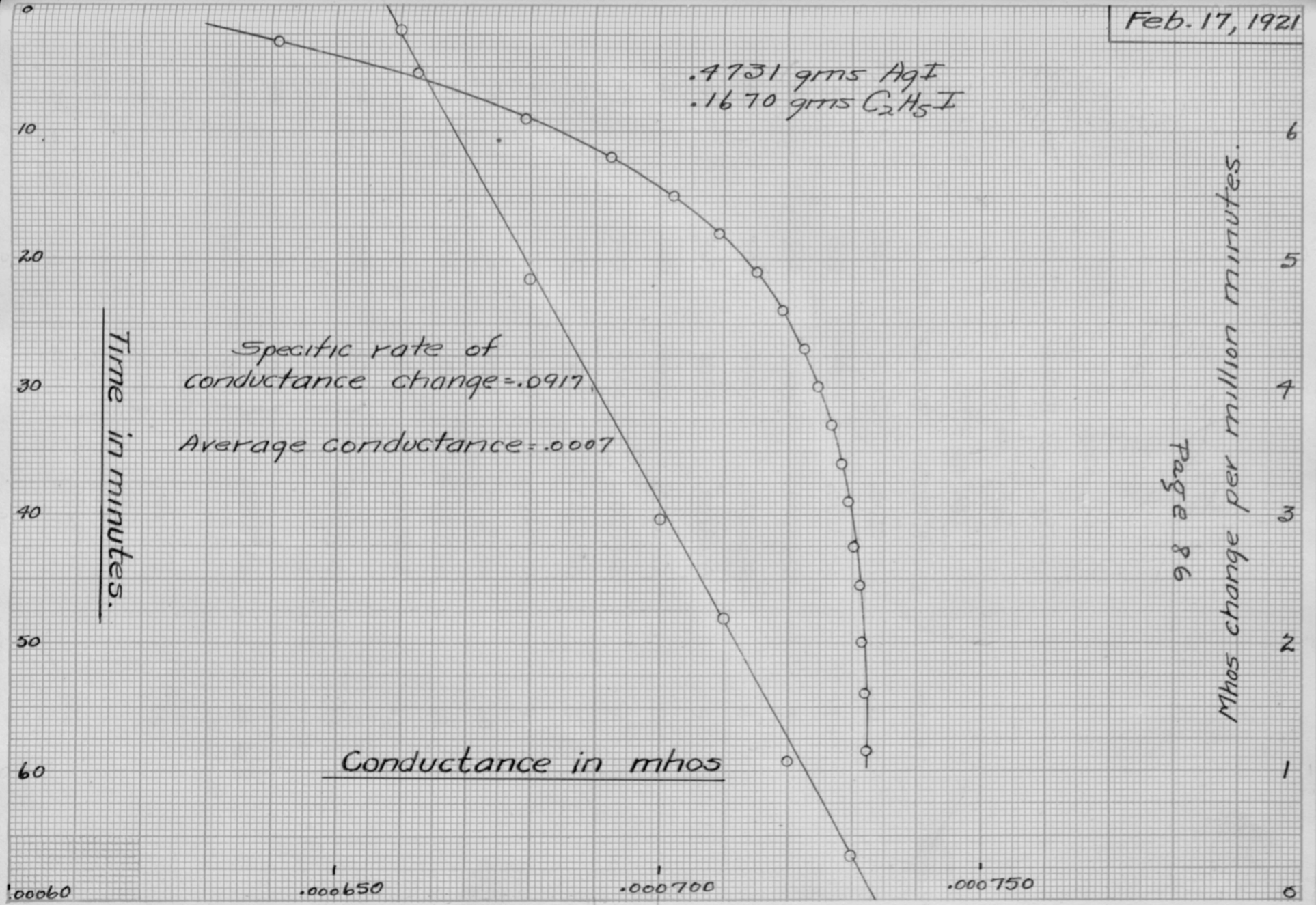
TIME	BOX RES.	BRIDGE	CONDUCTANCE	TIME
4:57	1410	4994		
58	1410	5000	.0007094	18
59	1410	5008		
5:00	1400	4997		
1	1400	5004	.0007151	21
2	1400	5008		
3	1390	49949		
4	1390	50000	.00071906	24
5	1389	50008		
6	1386	50017		
7	1383	49985	.00072295	27
8	1383	50005		
9	1381	50000		
10	1379	49995	.00072499	30
11	1378	50000		
12	1376	49996		
13	1376	50000	.00072690	33
14	1376	50020		

TIME	BOX RES.	BRIDGE	CONDUCTANCE	TIME
5:15	1375	50025		
16	1374	50024	.00072841	36
17	1372	49995		
18	1372	50015		
19	1371	50005	.00072956	39
20	1371	50015		
21	1371	50028		
22	1370	50020	.00073043	42
23	1369	50004		
24	1368	50010		
25	1366	50012	.00073163	45 1/2
26	1366	49970		
27	1366	49968		
28	1366	49970		
29	1366	49982		
30	1366	49990	.00073163	50
31	1366	49985		
32	1366	50000		

TIME	BOX RES.	BRIDGE	CONDUCTANCE	TIME
5:33	1366	50000		
34	1366	50000	.00073205	54
35	49995	49995		
36	1366	50004		
37	1366	50007		
38	1366	50010		
39	1365	49994	.00073241	58 1/2
401365	1365	50000		

SLOPE CURVE DATA

CONDUCTANCE	SLOPE	MHOS CHANGE PER MILLION MINUTES
.00066	$\frac{932}{276}$	6.79
.00068	$\frac{891}{368}$	4.85
.00070	$\frac{777}{520}$	2.98
.00071	$\frac{691}{630}$	2.195
.00072	$\frac{512}{951}$	1.077
.00073	$\frac{154}{88}$	.350


.4731 grms AgI
.1670 grms C_2H_5I
Specific rate of conductance change = .0917
Average conductance = .0007
Time in minutes.
Conductance in mhos
Mhos change per million minutes.
0
10
20
30
40
50
60
.00060
.000650
.000700
.000750
6
5
4
3
2
1
0

DATA

MARCH 16th, 1921.

.5079 gm C_2H_5I

.4559 gm AgI

TIME	BOX RES.	BRIDGE	CONDUCTANCE	TIME
4;40	862	5050	.001777	0
41	862	5085	.0018031	1
43	552	5005	.0018152	3
44	540	4969	.001829P	4
45	540	4985	.0018408	5
46	540	4999	.0018511	6
47	540	5004	.0018548	7
48	540	5011	.0018600	8
49	540	5023	.00186900	9
50	534	5001	.0018734	10
51	534	5009	.0018794	11
53	534	5020	.0018868	13
54	528	5001	.0018940	14 1/2
55	528	4998		
56	528	5006	.0018996	16 1/2
57	528	5009		
58	528	5011	.0019061	19
59	528	5018		
5:01	520	4981	.0019131	22
2	520	4988		

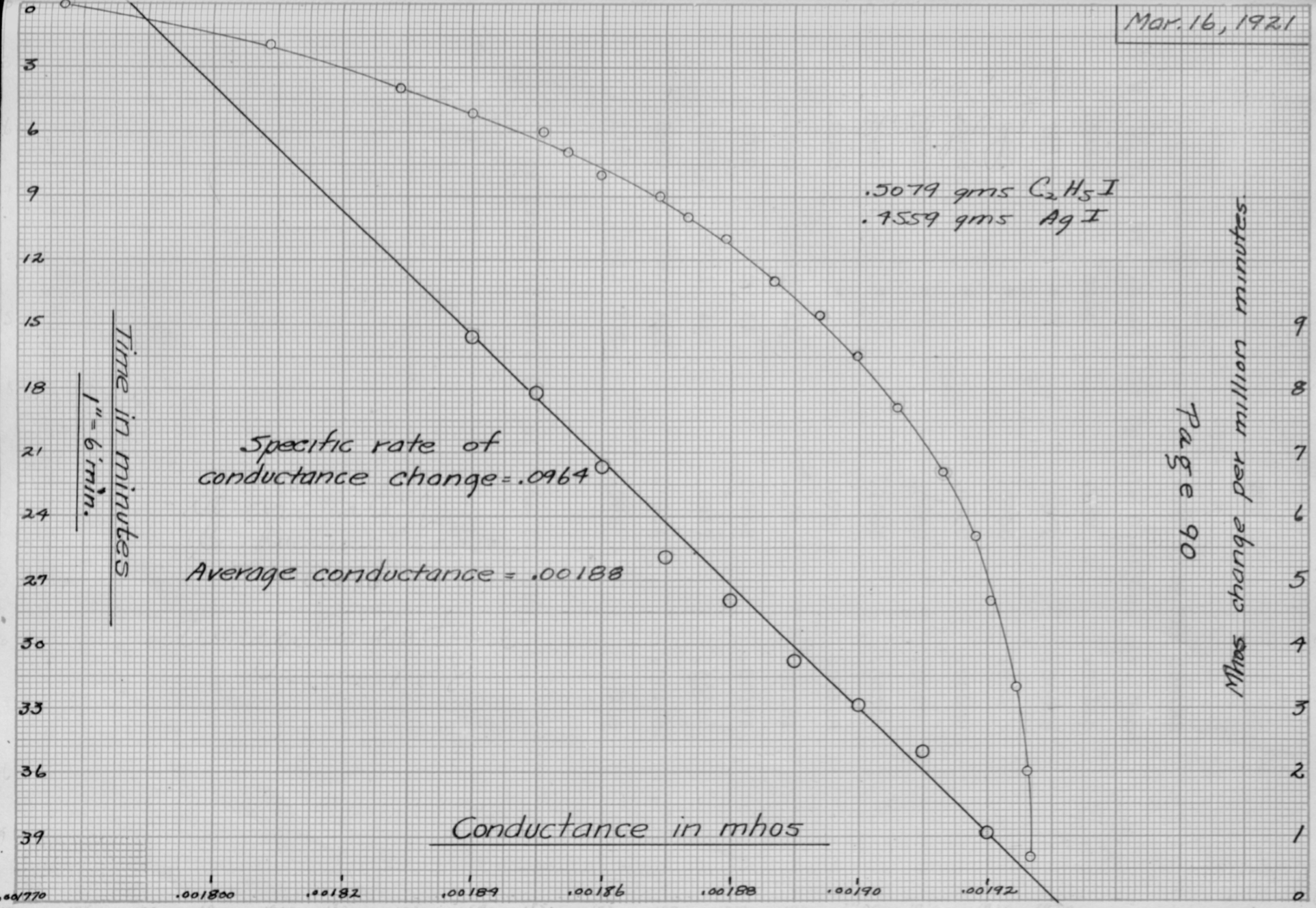
TIME	BOX RES,	BRIDGE	CONDUCTANCE		TIME
5:03	520	4991			
4	520	4994			
5	520	4994	.0019185		25
6	520	4993			
7	520	4994			
8	520	4998	.0019208		28
9	520	4999			
10	520	5000			
11	520	5001			
12	520	5002	.0019246		32
13	520	5002			
14	520	5004			
15	520	5003			
16	520	5004	.0019262		36
17	520	5005			
21	520	5005	.0019269	Final	37

SLOPE CURVE DATA

CONDUCTANCE	SLOPE	MHOS CHANGE PER MILLION MINUTES
.00184	$\frac{824}{308}$	8.82
.00185	$\frac{828}{347}$	7.95

CONDUCTANCE	SLOPE	MHOS CHANGE PER MILLION MINUTES.
.00186	$\frac{815}{402}$	6.77
.00187	$\frac{779}{486}$	5.36
.00188	$\frac{750}{533}$	4.70
.00189	$\frac{691}{616}$	3.74
.00190	$\frac{628}{686}$	3.051
.00191	$\frac{535}{772}$	2.315
.00192	$\frac{320}{101}$	1.052

Mar. 16, 1921



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SUMMARY OF RESULTS AS TAKEN FROM THE CURVES

Wt. C_2H_5I	Wt. added salt		Sp. Rate Cond Ch.	Av. Cond.
.5143	none		.925	.00145
.1510	"		.0872	.00025
.2801	"		.0950	.001
.0908	"		.0880	.00029
.5830	"		.0980	.0020
.8489	"		.1065	.0030
.2663	"		.090	.00108
.1590	.3515	KI	.103	.00181
.1312	.4070	KI	.0968	.00195
.1670	.4731	AgI	.0917	.0007
.5079	.4559	AgI	.0964	.00188
.1150	.1911	KNO_3	.093	.00106

The graph of this set of data follows.

Specific Conductance Change
Mhos change per minute, per mho
difference between instantaneous and
final conductance

AgI
KNO3
AgI
KI
KI

No catalyst was used
for points not labeled.

Average Conductance in mhos.

.0030 .0025 .002 .0015 .001 .0005

DISCUSSION OF THE EXPERIMENTS ON ETHYL IODIDE

The experimental results are summarized in the curves showing conductances plotted against time, and the accompanying slope curves, which give the best average value of a function to be called the specific rate of conductance change, and defined as the ratio of the instantaneous rate of change of conductance to the difference between the final and the instantaneous values of conductance. Conductances are measured in mhos, rates of change of conductance in mhos per million minutes, and the specific rate of conductance change in mhos change per minute, per mho difference between final and instantaneous values of conductance.

The treatment of the data was as follows. The Wheatstone bridge data was figured directly to conductances, no correction for resistances other than that of electrolyte being necessary, as the resistance of the whole system with a mercury short circuit between the electrodes was .059 ohms, which is entirely negligible in this work.
The data was averaged for intervals of a minute and a half to four minutes, and conductance plotted against time. At least the first twenty minutes the first twenty minutes was rejected. A triangle was then laid along the curve at several points, and the slope determined by counting squares. The recorded values are the mean of three closely agreeing values. The slopes were then calculated to mhos change in conductivity per million minutes by scale used in

plotting the conductance curve. This series of values was plotted against conductance, and the best straight line drawn through the points. Since the rate of change of conductance is zero when conductance reaches its final value, this line cuts the conductance axis at a sharp angle at the point representing final conductance, determining this final conductance more accurately than does the conductance vs. time curve, which approaches the final value of conductance asymptotically. Then, in effect, the instantaneous rates of change of conductance are plotted against the difference between the final and the instantaneous values of conductance, and the slope of the curve is the best average value of the specific rate of conductance change for the experiment under consideration.

Specific rates of conductance change were determined in this way for several initial concentrations of ethyl iodide, rangeing approximately from .02 N to .2 N. Similar determinations were made on mixtures containing some salt. The curve three pages back was plotted to represent the data for experiments in which only ethyl iodide was used. The other points, marked to indicate the particular salt used, were filled in later on the same sheet. The curve shows that there is no doubt but that the specific rate of conductance increases with conductance. It is therefore

necessary to examine critically all of the possible reasons for this change.

First, what is the effect of the equivalent conductivity of the electrolyte changeing with concentration? If conductance be represented by C, time by t and specific rate of conductance change by S, C_1 is the final value of conductance, and C_2 the instantaneous value.

$$S = \frac{\frac{dC}{dt}}{C_1 - C_2}$$

The term dt is independent of equivalent conductivity. $C_1 - C_2$ is obviously of the same dimensions as dC. C_2 is measured at the same point as dC, and as $C_1 - C_2$ decreases, it approaches dC in value. From these considerations, it is clear that whatever effect change of equivalent conductivity has on S, will be due to a change in C_1, the final value of the conductance. Since C_1 was measured in the more concentrated solution, it will be slightly too low in value, compared with C_2. But the effect of this difference must grow smaller and disappear when $dC = C_1 - C_2$, that is, at the end of the run. But the curves show that, within experimental error, the value of S is constant for a given run. Therefore, the observed increase in the value of S in solutions whose conductance

was high, cannot be due to the difference between the equivalent conductivity of the electrolyte in the different concentrations.

There is a possibility of there being a difference in the nature of the electrolyte among different runs; that is, a higher proportion of triethyl ammoniun ion might be present in the more concentrated solution, because of the mass-action effect of increased concentration of the corresponding amine. But it would be altogether unusual if the equivalent conductivity of the iodine salt of this ion were greater than that of ammonium iodide. The data of Franklin and Kraus, already referred to, shows that ammonium chloride has a slightly higher equivalent conductivity than do mono- and di- ethyl amine hydrochlorides. The supposition that the nature of the electrolyte changes with concentration is therefore discarded as improbable. It could be definitely settled if there were conductivity data for amine hydroiodide and ammonium iodide under the same conditions.

The measuring current is greater in concentrated solutions than in dilute, and its greater heating effect might raise the temperature thus causing the concentrated solution to show a higher conductance than it would at the proper temperature. In the absence of actual data as to the temperatures inside the cell, this possibility cannot be

denied. But conductivity never fell on letting stand with the current off after the reaction was practically complete, which furnishes pretty good evidence to the contrary. The last few readings of the run of December 21st, 1920 illustrate the point. It may of course be argued that this increase in condu ctance due to the last of the reaction, might have drowned out any effect of temperature. The answer is that it did and that any effect so small as to be drowned out by this slight change in conductivity is negligible.

Another possibility is that the rate of the reaction between ammonia andethyl iodide in the absence of any catalyzer, is not proportional to the concentration of ethyl iodide, but th the square or cube of it, and that the observed changes in the specific rate of conductance change are due to this. The data answers this question conclusively in the negative. If this were the case, as each reaction was nearly over, the rate of change would decrease as the square of the concentration of ethyl iodide decreased. The slope curves give absolutely no indication af this, as they certainly would do, espescially in the ranges where change of conductance was small and hence more nearly proportional to changes in concentration.

Another possibility is that variation from equality on the two sides of the zero of the current from the

high-frequency generator which furnished the measuring current was responsible, or that in some other way the electrical system was at fault. The only answer is, that the generator was tested by the manufactures and recommended as giving equality; and that the leads were kept as close together as possible all the way; and that during the latter part of the work, they were contained in a metallic conduit to sheild the circuit from the influence of any other circuit. It must be admitted that readings were not as definite on first atarting the generator as after a few minutes. No reason for this is assigned.

The above consideration seem to fairly well establish the conclusion that none of the assumptions so far made will explain the results observed, and, by elimination of these, that the increase in specific rate of conductance change is caused by the increased rate of formation of electrolyte in the solution, for a given concentration of ethyl iodide, when there is an electrolyte present. There are enough separate experiments with ethyl iodide alone to show that its reaction and altho there is less data for the other salts used, NH_4Br, KNO_3 and KI, the fact that the specific rates of conductance changes for the experiments in which these salts were used, lie close to the specific rates of conductance change for pure ethyl iodide and ammonia

of the same conductance, not to those for an equivalent concentration of ethyl iodide, seems to indicate that these salts are about as active catalyzers for the reaction as is the ammonium iodide formed in the reaction.

That the reaction of ammonia and ethyl iodide was autocatalytic was discovered first. This raised the question as to whether the ammonium ion, the iodine ion, undissociated iodide, ar all three of them were active. The experiments with ammonium bromide showed that it was practically the same as ammonium iodide in activity. Similarly for KI, used to teat the action of the iodine ion; and KNO_3, which was used to find out whether salts of neither iodine nor ammonium were active. Silver iodide was then tried out, as an easily solu ble salt which is slightly dissociated, excepting that if undissociated salt molecules were catalyzers for the reaction, that the specific rate of conductance change would be high; but no such effect was found. The results fell on the curve, just as the others had done; both the conductance and specific rate of conductance change were the same as if no AgI had been there.

The behavior here observed suggests an analogy between the catylytic effect of hydrogen ion on hydrolytic reactions, and of ammonium ion on ammonolytic reactions; and to a smaller degree between the effect of neutral salts in the two cases, No claim is made that the data in this paper

proves that catalysis of ammonolytic reactions is a specific property of ammonicm ion, as is the case of the catalysis of the hydrolysis of sugar by hydrogen ion in water solution; but neither does the data absolutely refute this possibility. If this is the case, however, the effect of neutral salts in increasing the activity of the ammonium ion ismore marked than is their effect on the activity of hydrogen ion in water solution, which is only about ten percent increase for an equivalquantity of the potassium salt of the respective acid. The effect of the neutral salt in these experiments, seems to be about the same as that of an equivalent quantity of ammonium salt. The only experiments run were a neutral salt was present, and ammonium salts absent, were those on the catalysis of the reaction of amyl oxalate and ammonia by sodium nitrate. Sodium nitrate alone seemed to have an about equal to that of an equivalent quantitn of ammonium salt; but these experiments were only roughly quantitative and should not form the basis of an opinion.

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is missing.

as proved that the increased rate of conductance change was due to a greater rate of reaction of a given concentration of ethyl iodide in liquid ammonia, if ammonium iodide, ammonium bromide, potassium iodide or potassium nitrate.

Curves are given which summarize the data and which show graphically what is here stated in words.

The question which the investigation was intended to solve, that of the possible equivalence of ammonium ion in liquid ammonia solution as a catalyzer for ammonolytic reactions, to hydrogen ion in water solution as a catalyzer for hydrolytic reactions, is still open.

In conclusion, the writer wishes to thank those who have made this work possible, and have always been ready with assistance and advice : Dr. H. P. Cady, whose idea furnished the topic for the investigation, and under whose direction the work was done; and Dr. H. M. Elsey, who designed and built all of the apparatus used, and who did all of the glass blowing which was so frequently necessary.

May 31, 1921 R. M. B.